



US006261691B1

(12) **United States Patent**
Atarashi et al.

(10) Patent No.: **US 6,261,691 B1**
(45) Date of Patent: **Jul. 17, 2001**

(54) **POWDER COATED WITH MULTILAYER COATING**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/202,210**

(22) PCT Filed: **Jun. 6, 1997**

(86) PCT No.: **PCT/JP97/01940**

§ 371 Date: **Apr. 14, 1999**

§ 102(e) Date: **Apr. 14, 1999**

(87) PCT Pub. No.: **WO97/47416**

PCT Pub. Date: **Dec. 18, 1997**

(30) **Foreign Application Priority Data**

Jun. 10, 1996 (JP) 8-147419

(51) Int. Cl.⁷ B32B 5/16

(52) U.S. Cl. 428/403
(58) Field of Search 428/403

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(57) **ABSTRACT**

A powder comprising a base particle which has been colored desirably and vividly and having a high light transmittance in the visible region. The powder is a multilayer-coated powder comprising a base particle having thereon a multilayered film comprising at least one thin layer comprising a metal sulfide, a metal fluoride, a metal carbonate or a metal phosphate. This multilayered film reflects or absorbs the light having a specific wavelength according to the thickness thereof, the sequence of layer superposition, etc.

14 Claims, 1 Drawing Sheet

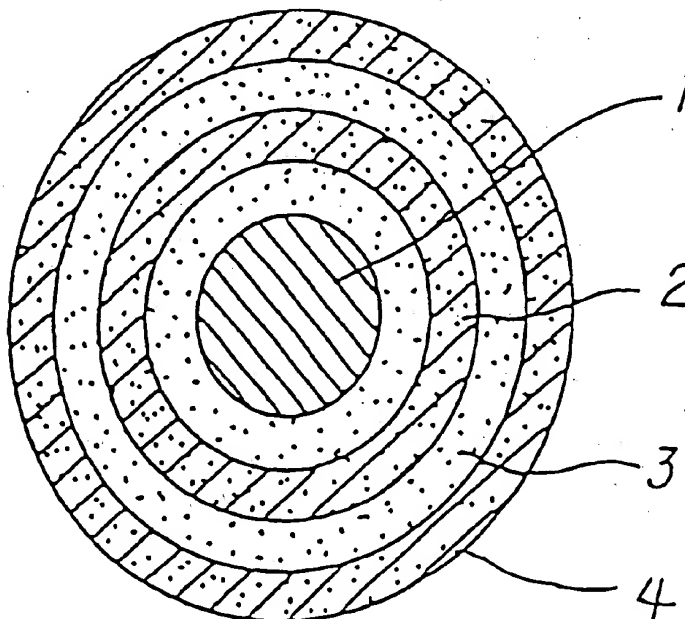
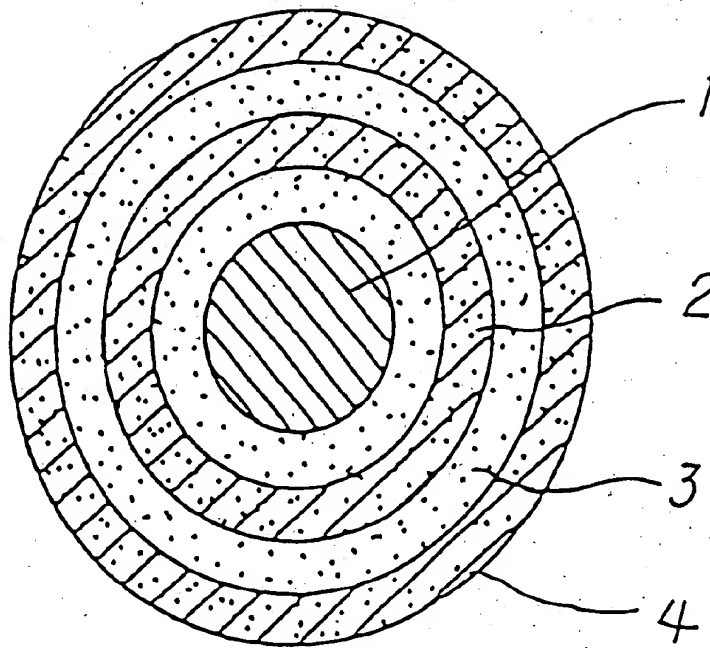


FIG. 1



POWDER COATED WITH MULTILAYER COATING

TECHNICAL FIELD

The present invention relates to a powder whose surface has been coated with a multilayered film. More particularly, this invention relates to a multilayer-coated powder suitable for use as a spherical spacer for liquid-crystal displays or a spherical lens for optical fibers and in magnetic coloring materials, such as magnetic color toners and magnetic color inks, retroreflective pigments, and cosmetics functioning to reflect ultraviolet and infrared rays.

BACKGROUND ART

A technique is known which comprises coating a powder with another substance to impart a new function thereto in order to use the powder in various applications.

For example, magnetic coloring materials for use in color electrophotography, etc., such as magnetic color toners and magnetic color inks, comprise magnetic particles as a base and coating films having various light reflection-absorption edges. The fine powders for use as spherical spacers for liquid-crystal displays or spherical lenses for optical fibers comprise a base particle comprising a transparent material, e.g., glass beads, and a light-transmitting film covering the surface thereof as a protective film. Some of the powders for use in cosmetics also comprise pigment particles whose surface has been coated with a substance which reflects ultraviolet and infrared rays.

As such a functional powder, the inventors previously proposed a powder comprising a base particle comprising a metal having thereon a metal oxide film having a uniform thickness and containing a metal different from the metal constituting the base particle (see Unexamined Published Japanese Patent Application No. 6-228604). According to this technique, a magnetic material, such as a metal (e.g., iron, cobalt, nickel), an alloy thereof, or iron nitride, is used as a base particle and two or more kinds of metal oxide films having different refractive indexes are formed thereon each in a thickness corresponding to one-fourth the wavelength of an incident light. Due to this constitution, a magnetic powder for magnetic toner is obtained which reflects all of the incident light and has a white color. Further forming a colored layer on the powder gives a magnetic color toner.

The inventors further improved the above powder and proposed a powder comprising a base particle and, formed thereon, not a combination of metal oxide films but plural layers of an oxide film and a metal film alternatively (see Unexamined Published Japanese Patent Application No. 7-90310). According to this technique, a multilayer-coated powder having excellent properties when used as a magnetic color toner or the like is obtained.

In recent years, further improvements in functions and a further reduction in particle size are required in the functional powders described above.

For example, in the field of color electrophotography, it is becoming necessary to obtain images having higher resolution and higher contrast. With this trend, magnetic color toners are required not only to have a reduced particle diameter to heighten resolution but also to be colored more vividly.

With respect to such requirements, a base particle can be colored desirably according to the above-described multilayer-coated powder proposed by the inventors, by superposing either oxide films or a combination of an oxide

film and a metal film on the surface of a base particle in such a manner that high-refractive-index films are disposed alternately with low-refractive-index films to thereby cause the coated particles to have an absorption peak at a specific wavelength or to conversely show exceedingly enhanced reflection in a specific wavelength range.

When the above multilayer-coated powder is applied to magnetic coloring material powders of the three primary colors, the cyan (blue) and yellow powders undoubtedly have improved vividness. However, in producing a powder colored in magenta, there have been cases where increasing the number of films especially for the purpose of obtaining a more vivid color results in a narrowed absorption bottom width, so that the resultant color as a whole is bluish. In application to a transparent white powder, it is important to reduce the scattering and reflection on the powder surface to thereby heighten transparency. However, the multilayer-coated powder described above is insufficient in this respect and it has been impossible to sufficiently color a transparent white powder.

These problems are thought to be attributable to the fact that in the above-described multilayer-coated powder proposed by the inventors because the film constitution is limited to a combination of metal oxides or a combination of metal oxides and metals, the range of refractive indexes obtainable in the whole multilayered film is limited and the delicate regulation of refractive index cannot be obtained.

Furthermore, the spherical lenses for use as spherical spacers for liquid-crystal displays, spherical lenses for optical fibers, or the like are required to have a high incident-light transmittance (transparency) on one hand and to have a reduced particle size on the other hand. However, the smaller the particle diameter, the more the reflective scattering is apt to occur on the surface and in the inner parts of the particles. Consequently, reduced particle diameters generally tend to result in reduced transparency.

A technique of heightening the purity of a substance constituting spherical lenses has conventionally been employed so as to obtain transparency. However, since there are differences in refractive index between each lens and substances adjacent thereto, interference occurs at these interfaces due to the differences in refractive index to provide new reflection sources. Thus, merely heightening the purity of the constituent substance brings about a limited improvement in the transparency of the spherical lenses.

For use in cosmetics and the like, powders are required to combine the function of effectively reflecting ultraviolet and infrared rays with the function of transmitting light in the visible region so as to enable the color of the pigment itself serving as a base particle to be observed. However, the conventional powders have been insufficient.

The present invention has been achieved in view of the circumstances described above. An object of the present invention is to provide a powder comprising a base particle which themselves has been colored desirably and having a high light transmittance in the visible region.

DISCLOSURE OF THE INVENTION

The above object is accomplished with the following powders according to the present invention:

- (1) A multilayer-coated powder comprising a base particle having thereon a multilayered film comprising at least one thin layer comprising a metal sulfide, a metal fluoride, a metal carbonate or a metal phosphate, wherein the metal in the metal fluoride, metal carbonate or metal phosphate is an alkali metal or an alkaline earth metal, and the multilayered film reflects a specific wavelength;

(2) A multilayer-coated powder comprising a base particle having thereon a multilayered film comprising at least one thin layer comprising a metal sulfide, a metal fluoride, a metal carbonate or a metal phosphate, wherein the metal in the metal fluoride, metal carbonate or metal phosphate is an alkali metal or an alkaline earth metal, and the multilayered film transmits light in the visible region.

Since the substances constituting the multilayered film in the above constitutions differ from each other in refractive index, the multilayered film as a whole can be made to reflect the light having a specific wavelength or completely transmit the light or incident light having a specific wavelength by suitably changing the thickness of the film or the sequence of layer superposition.

Consequently, by applying the above multilayered film to a base particle of any of various kinds, a functional powder is obtained which has the function possessed by the base particle and which has been colored desirably or is transparent.

For example, when a base particle made of a magnetic material is used, a magnetic color toner colored vividly can be obtained. When a base particle made of a glass or transparent resin is used, spherical lenses can be obtained which have high transparency and are suitable for use as spherical spacers for liquid.

The substances usable for constituting the multilayered film in the present invention are metal sulfides, metal fluorides, metal carbonates, and metal phosphates.

Metal sulfides have a refractive index higher than metal oxides. Specifically, the refractive index of cadmium sulfide is 2.6 and that of zinc sulfide is from 2.3 to 2.4.

Metal fluorides have a low refractive index which cannot be obtained with metal oxides. Especially preferred are the fluorides of alkali metals or alkaline earth metals.

Specifically, the refractive index of calcium fluoride is 1.23 to 1.26; that of sodium fluoride is 1.34; that of trisodium aluminum fluoride is 1.35; that of lithium fluoride is 1.37; and that of magnesium fluoride is 1.38.

Metal phosphates or metal carbonates have refractive indexes intermediate between those of the metal sulfides and those of the metal fluorides. Especially preferred are the phosphates or carbonates of alkali metals or alkaline earth metals. Due to the use of these metal phosphates or metal carbonates, the choice of films can be widened and the refractive indexes of the whole multilayered film can be regulated delicately to attain a combination of more various refractive indexes.

Specifically, the refractive index of calcium phosphate is 1.6; that of sodium phosphate is 1.58; that of cerium phosphate is 1.8; and that of lanthanum phosphate is 1.8. The refractive index of calcium carbonate is 1.66; that of magnesium carbonate is 1.6 to 1.7; that of barium carbonate is 1.6; and that of strontium carbonate is from 1.5 to 1.6.

It is possible to add metal chalcogenides other than the above-described metal sulfides, and metal oxides to the film materials. In this case, the metals are not particularly limited, and ones having a desired refractive index can be suitably selected.

Examples of the metal chalcogenides include metal tellurides and metal selenides. The refractive indexes of these chalcogenides are roughly in the range of 2.4 to 3.0, although they vary depending on to the kinds of the metals.

Examples of the metal oxides include those given in Unexamined Published Japanese Patent Applications Nos. 6-22286 and 7-90310, both filed by the present inventors. However, the metal oxides should not be construed as being

limited thereto. The refractive indexes of the metal oxides are roughly in the range of 1.8 to 2.6, although they vary depending on the kinds of the metals.

If necessary, films of metals selected, for example, from silver, cobalt, nickel, iron, and alloys thereof may be further added.

By the use of these films, the multilayered film can be regulated so as to have more various refractive indexes.

For forming films comprising the above-described metal sulfides, metal fluorides, metal carbonates, and metal phosphates, the following methods are preferably used, which are advantageous from the standpoints of film evenness and film thickness regulation:

A. Film formation by solid deposition in liquid phase;

B. Film formation in vapor phase (CVD and PVD).

Film formation by these methods can be conducted according to known steps using conditions suitably selected for each step according to the material.

In the case of adding a metal oxide film, it is preferred to use the film-forming method using a metal alkoxide which is described in Unexamined Published Japanese Patent Applications Nos. 6-22286 and 7-90310, both filed by the present inventors.

In the case of adding a metal film, it can be formed by electroless plating or contact electroplating or by sputtering. However, the thickness of a film formed by contact electroplating or sputtering may vary from particle to particle, because there are cases where in the contact electroplating, powder particles not in contact with an electrode are not plated, and in the sputtering, a metal vapor does not evenly collide against the powder particles. Consequently, film formation by electroless plating is preferred.

In the film-forming methods described above, films are designed in the following manner.

Coating films differing in refractive index are alternately formed on each base particle so as to satisfy the following equation (1). Namely, coating films which each is made of a substance having a refractive index n and has a thickness d corresponding to m (integer) times the value which is one-fourth a wavelength of visible light are formed in an appropriate thickness and number. As a result, the light having a specific wavelength λ (the light utilizing Fresnel's interference reflection) is reflected or absorbed.

$$nd = m\lambda/4 \quad (1)$$

By utilizing this principle to conduct a film design, it is possible to form a film which reflects the light having specific wavelengths to develop the color corresponding to the reflected light. Alternatively, a film which transmits incident light throughout its wavelength range and which is hence transparent can be formed.

In actual film formation, the film thickness of each layer is designed while determining the change of optical film thickness, which is the product of the refractive index of the film and the film thickness, as a reflection waveform by means of a spectrophotometer or the like so that the reflection waveform conforms to the waveform of a target color. For example, when a multilayered film is constituted of unit coating films which have reflection waveform peaks located apart from each other in two or more positions throughout the visible region, the multilayered film is a white film which wholly reflects the visible light. When the unit coating films are regulated so that the reflection waveform peaks thereof are in exactly the same position, the multilayered film can be monochromatically colored in, e.g., blue, green, or yellow, without using a dye or pigment.

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Furthermore, a transparent film can also be obtained by reducing the reflectance to an exceedingly low level.

On the other hand, the base particle in the present invention can be selected from various materials according to the purposes thereof. That is, a powder coated with the multilayered film described above is a functional powder which has the function possessed by the base particle and which has been colored desirably or is transparent.

For example, when a magnetic material is used as a base material, a magnetic color toner colored vividly can be obtained. When a base particle made of a glass or transparent resin is used, spherical lenses can be obtained which have high transparency and are suitable for use as spherical spacers for liquid-crystal displays, spherical lenses for optical fibers, etc. Furthermore, when a pigment is used as a base particle, a cosmetic functioning to reflect ultraviolet and infrared rays can be obtained.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 diagrammatically illustrates, by means of a sectional view, the structure of a particle of a multilayer-coated powder according to the present invention. This particle contains a base particle 1 as a core and is constituted by successively superposing, on the surface of the core, films 2, 3, and 4 each selected from metal sulfides, metal fluorides, metal carbonates, and metal phosphates and regulated so as to have a specific thickness.

MODES FOR CARRYING OUT THE INVENTION

The present invention can be understood more clearly by reference to the following Examples. However, the invention should not be construed as being limited by these Examples in any way.

EXAMPLE 1

(transparent powder)

Fifty grams of glass beads (average particle diameter, 33 μm) were dispersed into an aqueous solution prepared beforehand by dissolving 11.3 g (0.25 mol/l) of calcium chloride in 600 ml of water. A solution prepared beforehand by dissolving 20 g of calcium carbonate in 600 ml of water was gradually added dropwise to the dispersion under stirring over 1 hour.

After the dropping, the solution was allowed to react while maintaining the temperature of the solution at 60° C. After completion of the reaction, the reaction mixture was washed with a sufficient amount of deionized water with decantation, and the solid matter was then separated by filtration. The calcium carbonate-coated powder obtained was dried and heated in a vacuum dryer at 180° C. for 8 hours.

The powder thus obtained had a calcium carbonate film (refractive index, 1.65) formed on the glass beads, and the thickness of the film was 278 nm.

Subsequently, 40 g of the calcium carbonate-coated powder was added to a solution prepared by dissolving 12.8 g of zircon butoxide in 200 ml of isopropanol. A solution prepared by mixing 3.7 g of water with 25 g of propanol was added dropwise over 1 hour to the above solution under stirring while maintaining the solution at 55° C.

After the dropping, the mixture was allowed to react for 7 hours. The resultant reaction mixture was washed with a sufficient amount of propanol with decantation. The solid matter was taken out by filtration and then dried and heated in a vacuum dryer at 180° C. for 8 hours.

Thus, a zirconia-calcium carbonate-coated powder was obtained. The zirconia film (refractive index, 2.10) of this zirconia-calcium carbonate-coated powder had a thickness of 143 nm.

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Furthermore, 20 g of the zirconia-calcium carbonate-coated powder was stirred in a rotating fluidized bed in vacuo. Simultaneously with the stirring, a tungsten board disposed in the rotating fluidized bed apparatus and filled with a magnesium fluoride powder was heated. A vapor of magnesium fluoride was thus generated to treat the coated powder for 2 hours to thereby obtain a magnesium fluoride-zirconia-calcium carbonate-coated powder. The magnesium fluoride film (refractive index, 1.38) of this magnesium fluoride-zirconia-calcium carbonate-coated powder had a thickness of 109 nm.

The thus-obtained glass beads coated with the three layers had a considerably reduced reflectance of 0.7% or less in the range of 380 nm to 780 nm. Probably, this is because the glass beads had been reduced in scattering by the formation of the multilayered film.

EXAMPLE 2

(purple magnetic pigment)

First Layer: Silica Film:

Into 500 ml of ethanol was dispersed 50 g of a carbonyl iron powder (average particle diameter, 1.8 μm) manufactured by BASF. Thereto were added 20 g of silicon ethoxide, 15 g of ammonia water (29%), and 20 g of water. This mixture was allowed to react for 5 hours under stirring. After the reaction, the reaction mixture was diluted and washed with ethanol and filtered. Thereafter, the solid matter was dried in a vacuum dryer at 110° C. for 3 hours. After the drying, the resultant powder was heated with a rotary tubular oven at 650° C. for 30 minutes to obtain silica-coated powder A.

After the heating, 40 g of the silica-coated powder A obtained was redispersed into 400 ml of ethanol. Thereto were added 12 g of silicon ethoxide and 16 g of ammonia water (29%). This mixture was allowed to react for 5 hours, and then dried in vacuo and heated in the same manner as in the first coating. Thus, silica-coated powder B was obtained.

The silica-coated powder B obtained had satisfactory dispersibility and was an independent particle. The silica film (refractive index, 1.51) formed on the surface of the carbonyl iron powder had a thickness of 300 nm.

Second Layer: Zinc Sulfide Film:

To a solution prepared beforehand by dissolving 1.34 g of zinc ethoxide was added 30 g of the silica coated powder B. Hydrogen sulfide gas was fed thereto under stirring at a rate of 3 ml/min to conduct bubbling for 3 hours. The resultant reaction mixture was diluted and washed with a sufficient amount of ethanol, dried in a vacuum dryer for 1 hour, and then heated with a rotary tubular oven at 650° C. for 30 minutes to obtain a zinc sulfide-silica-coated powder.

The zinc sulfide-silica-coated powder obtained had satisfactory dispersibility and was an independent particle. This zinc sulfide-silica-coated powder had a spectral reflection curve having a peak wavelength of 770 nm and had a reflectance at the peak wavelength of 50%. It was vivid yellow. The zinc sulfide film (refractive index, 2.3) of the zinc sulfide-silica-coated powder had a thickness of 12 nm.

Third Layer: Magnesium Fluoride Film:

Twenty grams of the zinc sulfide-silica-coated powder was stirred in a rotating fluidized bed in vacuo. Simultaneously with the stirring, a tungsten board disposed in the rotating fluidized bed apparatus and filled with a magnesium fluoride powder was heated. A vapor of magnesium fluoride was thus generated to treat the coated powder for 2 hours to thereby obtain a magnesium fluoride-zinc sulfide-silica-coated powder.

The magnesium fluoride film (refractive index, 1.38) of the magnesium fluoride-zinc sulfide-silica-coated powder had a thickness of 124 nm.

The carbonyl iron powder obtained through coating with the three layers had an absorption bottom at 525 nm, at which the reflectance was 15%. The difference between this reflectance and a maximum reflectance of 60% (780 nm) was 35%. It was vivid purple.

INDUSTRIAL APPLICABILITY

As described above, since the substances constituting the multilayered film in the present invention differ from each other in refractive index, the multilayered film as a whole can be made to reflect the light having a specific wavelength or completely transmit the light or incident light having specific wavelengths by suitably changing the thickness of the film or the sequence of layer superposition.

Consequently, by applying the above multilayered film to a base particle of any of various kinds, a functional powder is obtained which has the function possessed by the base particle and which has been colored vividly or is transparent.

For example, when a base particle made of a magnetic material is used, a magnetic color toner colored vividly can be obtained. When a base particle made of a glass or transparent resin is used, spherical lenses can be obtained which have high transparency and are suitable for use as spherical spacers for liquid-crystal displays, spherical lenses for optical fibers, etc. Furthermore, when a pigment is used as a base particle, a cosmetic functioning to reflect ultraviolet and infrared rays can be obtained.

What is claimed is:

1. A multilayer-coated powder comprising a base particle having thereon a multilayered film comprising at least one metal sulfide layer and at least one layer selected from the group consisting of a metal fluoride, a metal carbonate and a metal phosphate, wherein the metal in the metal fluoride, metal carbonate or metal phosphate is an alkali metal or an alkaline earth metal, the multilayered film reflects a specific wavelength, and each layer of the multilayered film has a different refractive index.

2. The multilayer-coated powder according to claim 1, wherein the metal sulfide is selected from the group consisting of zinc sulfide and cadmium sulfide.

3. The multilayer-coated powder according to claim 1, wherein the base particle is spherical.

4. A multilayer-coated powder comprising a base particle having thereon a multilayered film comprising at least one layer comprising a metal sulfide, a metal fluoride, a metal carbonate or a metal phosphate, wherein the metal in the metal fluoride, metal carbonate or metal phosphate is an alkali metal or an alkaline earth metal, the multilayered film transmits light in the visible region, and each layer of the multilayered film has a different refractive index.

5. The multilayer-coated powder according to claim 4, wherein the multilayered film comprises a metal sulfide layer and at least one layer selected from the group consisting of a metal fluoride, a metal carbonate and a metal phosphate, said metal in the metal fluoride, metal carbonate and metal phosphate is an alkali metal or an alkaline earth metal.

6. The multilayer-coated powder according to claim 4, wherein the metal sulfide is selected from the group consisting of zinc sulfide and cadmium sulfide.

7. The multilayer-coated powder according to claim 4, wherein the base particle is spherical.

8. A multilayer-coated powder comprising a base particle having thereon a multilayered film comprising at least one layer comprising a metal sulfide selected from the group consisting of zinc sulfide and cadmium sulfide, a metal fluoride, a metal carbonate or a metal phosphate, wherein the metal in the metal fluoride, metal carbonate or metal phosphate is an alkali metal or an alkaline earth metal, the multilayered film reflects a specific wavelength, and each layer of the multilayered film has a different refractive index.

9. The multilayer-coated powder according to claim 8, wherein the base particle is spherical.

10. A multilayer-coated powder comprising a base particle having thereon a multilayered film comprising at least one metal sulfide layer and at least one layer selected from the group consisting of a metal fluoride, a metal carbonate and a metal phosphate, wherein the metal in the metal fluoride, metal carbonate or metal phosphate is an alkali metal or an alkaline earth metal, the multilayered film transmits light in the visible region, and each layer of the multilayered film has a different refractive index.

11. The multilayer-coated powder according to claim 10, wherein the metal sulfide is selected from the group consisting of zinc sulfide and cadmium sulfide.

12. The multilayer-coated powder according to claim 10, wherein the base particle is spherical.

13. A multilayer-coated powder comprising a base particle having thereon a multilayered film comprising at least one layer comprising a metal sulfide selected from the group consisting of zinc sulfide and cadmium sulfide, a metal fluoride, a metal carbonate or a metal phosphate, wherein the metal in the metal fluoride, metal carbonate or metal phosphate is an alkali metal or an alkaline earth metal, the multilayered film transmits light in the visible region, and each layer of the multilayered film has a different refractive index.

14. The multilayer-coated powder according to claim 13, wherein the base particle is spherical.

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US005225186A

United States Patent [19]

Castrogiovanni et al.

[11] Patent Number: 5,225,186
[45] Date of Patent: Jul. 6, 1993

[54] HIGH COSMETIC POWDER LIPSTICK COMPOSITION

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[21] Appl. No.: 705,217

[22] Filed: May 24, 1991

Related U.S. Application Data

[63] Continuation of Ser. No. 541,612, Jun. 21, 1990, abandoned.

[51] Int. Cl.³ A61K 7/025

[52] U.S. Cl. 424/64; 424/63;
424/DIG. 5

[58] Field of Search 424/64, 70, 63, 59,
424/DIG. 5, 69, 401

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[57] ABSTRACT

A stick shaped lipstick composition which comprises a higher loading of cosmetic powders than those available in prior art compositions is disclosed. The composition includes between about 10% and about 65% of at least one cosmetic powder. At least one low viscosity liquid carboxylic acid ester, present in a concentration of between about 10% and about 65%, is also included. A third component of the composition is at least one high viscosity surface oil included in an amount of between about 1% and about 18%. The composition additionally comprises between about 2% and about 15% of at least one plasticizing agent. All of the above mentioned percentages are by weight, based on the total weight of the composition. The high concentration of cosmetic powder provides a unique finish, texture and feel lipstick heretofore unavailable in convenient stick shape.

11 Claims, No Drawings

HIGH COSMETIC POWDER LIPSTICK COMPOSITION

This is a continuation of copending application(s), Ser. No. 07/541,612 filed on Jun. 21, 1990, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to stick shaped lipstick cosmetic products which are designed to provide relatively high concentrations of powdered components and which provide both the unique finish (visual appearance), texture and feel of a pressed powder cosmetic product.

Stick shaped lip cosmetic products have been molded or produced in a variety of shapes and sizes ranging from slimline versions to the standard size bullet configuration. A common limitation of the prior art lipstick formulations, however, has been the relatively low amount of cosmetic powder materials that can be readily incorporated into such products. Incorporating powders at levels of about 20% to 30% by weight or more into prior art stick products has generally resulted in poor moldability, poor structure and poor product comfort or performance for the user.

At the present time, commercially available lip powders have been limited to those that are marketed in other than a stick shaped configuration. Lip powder products on the market today are typically presented in a pressed powder compact form to be applied with an applicator. This compact form of lip product is limiting and is not as generally accepted for use as the stick form of lip product, i.e., lipstick. Therefore, there is a need for a stick product that will apply cosmetic powders to the lips and thereby provide finishes that were heretofore theoretically obtainable only in pressed powder compact form.

An object, therefore, of the present invention is to provide a stick shaped lipstick product which has a relatively high content of cosmetic powder.

A further object of the present invention is to provide a stick shaped lipstick product which will provide finishes to the lips that have, heretofore, only been available from pressed powder products.

2. Description of the Prior Art

Japanese Patent Application 61257908 to Shiseido KK, published Nov. 15, 1986 discloses a make-up cosmetic composition, which may be a lipstick, which employs therein certain two-component powdery materials formed from an organic particulate or an inorganic nucleus material having a particle size of 1-100 microns, which nucleus material is coated with a particulate organic or inorganic powder material, such second particulate material having a particle size 1/5 that of such first particulate material.

U.S. Pat. Nos. 4,659,562 and 4,820,510 disclose cosmetic make-up compositions containing finely divided silica and finely divided polyethylene fibers.

Japanese Patent Application 56081512 to Sakata KK, published Jul. 3, 1981 discloses a cosmetic material which contains porous globular granules, the surface of which has been rendered lyophobic.

SUMMARY OF THE INVENTION

The present invention relates to a stick shaped lipstick product which comprises a high concentration of

cosmetic powder components and a selected combination of other components designed to enable the final formulation to be molded into a stick shaped configuration that provides powder-type finishes to the lips.

In accordance with the present invention a stick shaped lipstick composition is provided. The lipstick composition comprises between about 15% and about 80% of at least one cosmetic powder; between about 10% and about 65% of at least one low viscosity liquid carboxylic acid ester; between about 1% and about 18% of at least one high viscosity surface oil; and between about 2% and about 15% of at least one plasticizing agent, all said percentages being by weight, based on the total weight of the lipstick composition.

DETAILED DESCRIPTION

The stick shaped lipstick composition of the present invention includes between about 15% and about 80%, which, it should be appreciated, denotes percentage by weight, based on the total weight of the composition, of at least one cosmetic powder. Preferably, the cosmetic powder constituent of the composition represents between about 25% and about 45% by weight of the composition.

Cosmetic powders within the contemplation of the present invention include mica, talc, bismuth oxychloride, bentonite, nylon, silica, acrylates copolymer and mixtures thereof. It should be understood that the above recited cosmetic powders encompass all materials within the meaning of those names as set forth in the CTFA Cosmetic Ingredient Dictionary, Third Edition, published by the Cosmetic, Toiletry and Fragrance Association, Inc., Washington, D.C. (1982), which is incorporated herein by reference. For example, mica, as defined in the CTFA Cosmetic Ingredient Dictionary, 3rd Ed., includes uncoated mica as well as titanated mica, that is, mica coated with titanium dioxide.

It is emphasized that the CTFA Cosmetic Ingredient Dictionary, Third Edition in defining mica as including titanated mica, that is, mica coated with titanium dioxide, emphasizes that not only may the cosmetic powder constituent be comprised of mica in whole or in part but, also, that the cosmetic powder component of the lipstick composition may be wholly or partially titanated mica. Those skilled in the art are aware that titanated mica provides a "frost" appearance that many users find attractive.

A recently approved CTFA ingredient not included in the aforementioned CTFA Cosmetic Ingredient Dictionary, Third Edition, that is within the contemplation of the cosmetic powder component, useful in the present lipstick composition, is teflon. It is anticipated that this ingredient will be included in the next published edition of the Dictionary.

In a preferred embodiment, some or all of the cosmetic powder included in the lipstick composition may be coated with a hydrophobic agent. The hydrophobic agent coating of some or all of the cosmetic powder component not only imparts hydrophobicity, a desirable attribute for a lipstick, but, in addition, provides the lipstick composition with smoother texture and improves the lipstick composition's moisturization characteristic.

In the preferred embodiment wherein the cosmetic powder is coated with a hydrophobic agent, the degree of coating is such that the hydrophobic agent comprises between about 1% and about 5% by weight, based on the total weight of the hydrophobic coated cosmetic

powder. More preferably, the concentration of the hydrophobic agent is in the range of between about 1.5% and about 3% by weight.

Among the hydrophobic agents preferred for use in coating the cosmetic powders within the contemplation of the stick lipstick composition are 6-aminocaproic acid, lecithin, a mixture of cyclomethicone and mineral oil, preferably a 1:99 weight mixture of mineral oil to cyclomethicone. Again, these hydrophobic agents are set forth in the CTFA Cosmetic Ingredient Dictionary, 3rd Ed., incorporated herein by reference.

The cosmetic powder component of the stick lipstick composition, independent of its identity, whether it is coated or not, is preferably characterized by a particle size of less than about 30 microns. More preferably, the particle size of the cosmetic powder component is in the range of between about 1 micron and about 25 microns.

Another essential component of the stick shaped lipstick composition is at least one liquid, low viscosity carboxylic acid ester. The ester component, present in the composition in a concentration of between about 10% and about 65% by weight, based on the total weight of the lipstick composition, is preferably characterized by a viscosity, at 25° C., in the range of between about 5 centipoise (cp) and about 100 cp. More preferably, the liquid low viscosity carboxylic acid ester is present in a concentration of between about 25% and about 45% by weight.

The carboxylic acid ester component serves to wet out the cosmetic powder component and significantly contribute to the light, dry, silky and powdery texture of the final lipstick product. In addition, the liquid ester component performs in such a way to promote better adhesion and wear of the lipstick composition to the lips of the user. The ester component further contributes to the moisturizing effect of the lipstick composition on the lips to which it is applied.

Among the liquid, low viscosity carboxylic acid esters that can be used in the lipstick composition are isotridecyl isononanoate, isostearyl neopentanoate, cetyl octanoate, glyceryl trioctanoate, isodecyl oleate and isodecyl neopentanoate, ingredients mentioned in the CTFA Ingredient Dictionary, 3rd Edition incorporated herein by mentioned reference. In addition, mixtures of these esters, as well as PEG-4 diheptanoate, tridecyl neopentanoate, isohexyl neopentanoate and tridecyl octanoate, ingredients which are not included in the Third Edition but will appear in the next edition of the CTFA Ingredient Dictionary, can be used with each other or with one or more of the esters, recited above, already included in the 3rd Edition, to provide the ester component of the lipstick composition.

A third critical ingredient of the lipstick composition is at least one high viscosity surface oil. The surface oil component comprises one or more surface oils which are characterized by a viscosity, at 25° C., in the range of between about 200 cp. and about 250,000 cp. The surface oil component contributes emolliency to the lipstick composition. To that end, the surface oil component comprises between about 1% and about 18% by weight of the total weight of the lipstick composition. More preferably, the surface oil component comprises between about 3% and about 10% by weight of the total composition.

The surface oils employable as the surface oil component of the lipstick composition of the present invention include castor oil, lanolin, sorbitan sesquioleate and mixtures thereof. These ingredients are fully defined in

the aforementioned CTFA Cosmetic Ingredient Dictionary, 3rd Ed., incorporated herein by reference. In addition to these surface oils, another such oil, triisocetyl citrate, which will appear in the next edition of the Dictionary, may be utilized alone or with one or more of the surface oils mentioned above.

A fourth and last essential component of the lipstick of the present invention is a plasticizing agent. The plasticizing agent aids in providing smoothness to the lipstick composition, plasticizing as it does the hard components contained therein.

To provide this effect, at least one plasticizing agent is included in the lipstick composition in a concentration in the range of between about 2% and about 15% by weight based on the total weight of the lipstick composition. More preferably, the plasticizing component represents between about 5% and about 12% by weight of the lipstick composition.

Among the plasticizers contemplated for use in the lipstick composition are a mixture of acetylated lanolin alcohol and cetyl acetate, caprylic/capric triglyceride, oleyl alcohol, lanolin alcohol, octyldodecanol and mixtures thereof. Definitions of these preferred plasticizers are provided by the CTFA Cosmetic Ingredient Dictionary, Third Ed., incorporated herein by reference.

Of these plasticizers, a mixture of acetylated lanolin alcohol and cetyl acetate is particularly preferred for use in the lipstick composition. Still more preferably, an admixture of between about 10% and about 30% by weight, based on the total weight of the admixture, of acetylated lanolin alcohol and between about 70% and about 90% by weight, again based on the total weight of the admixture, cetyl acetate is utilized as the plasticizer component.

In a preferred embodiment the lipstick composition includes spherical silica. It should be appreciated that spherical silica, which has not yet been included in the CTFA Cosmetic Ingredient Dictionary but has been approved for use in cosmetic applications and thus will appear in the next edition of the Dictionary, has an average particle size of between about 1 micron and about 20 microns. More preferably, in the preferred embodiment wherein spherical silica is included in the lipstick composition, it is present in an average particle size range of between about 3 microns and about 15 microns.

The inclusion of spherically shaped silica is preferred in that it significantly increases the ease of application of the lipstick. Those skilled in the art are aware of a major detriment to the use of high cosmetic powder-containing lipsticks in the prior art has been the difficulty of application. Lipstick compositions in the prior art which comprised high concentrations of cosmetic powders tended to be dry and scratchy, causing irritation upon application. The inclusion of spherical silica provides a "rollerball" effect minimizing friction, thus promoting ease of application of a powdered product to the lips. Spherical silica also is believed to selectively absorb oils both in the product and on the lips which helps facilitate controlled application and quality of wear (i.e. minimal bleeding and feathering).

In the preferred embodiment wherein spherical shaped silica is incorporated in the lipstick composition it is preferably present in a concentration in the range of between about 0.5% and about 20% by weight, based on the total weight of the lipstick composition. More preferably, the spherical shaped silica constituent is

present in the range of between about 1% and about 10% by weight of the composition.

Another preferred ingredient of the lipstick composition is wax. Wax is provided to provide structural stability by binding, solidifying and hardening the other components of the composition. In the preferred embodiment wherein a wax component is incorporated into the lipstick composition it is present in a concentration of between about 5% and about 20% by weight, based on the total weight of the lipstick composition. More preferably, the wax constituent comprises between about 9% and about 15% by weight.

Among the waxes that can be employed as the wax constituent of the lipstick composition are carnauba, ceresin, PEG-20 sorbitan beeswax, paraffin, microcrystalline wax, glyceryl tribehenate, candelilla wax and mixtures thereof. Each of these components are included and defined in the CTFA Cosmetic Ingredient Dictionary, Third Edition, incorporated by reference.

Another preferred ingredient of the lipstick composition is a pigment component. One or more pigments, providing between about 0.5% and about 10% by weight of the total composition, is preferably included to provide the desired color shade to the lipstick composition. More preferably, the pigment constituent represents between about 1% and about 7% by weight of the lipstick composition.

Among the preferred ingredients within the contemplation of the pigment component are iron oxides, D&C Red No. 7 calcium lake, D&C Red No. 6 barium lake, D&C Red No. 27 aluminum lake, D&C Red No. 33 aluminum lake, D&C Red No. 30 lake, FD&C Yellow No. 6 aluminum lake, FD&C Blue No. 1 aluminum lake, D&C Orange No. 5, D&C Red No. 21 and D&C Red No. 27. One or a mixture of two or more of these pigments is preferably utilized in the lipstick composition.

It should be appreciated that each of these pigments is defined in the CTFA Cosmetic Ingredient Dictionary, Third Edition incorporated herein by reference. Furthermore, it should also be understood that iron oxides and selected organic colorants of choice may be included in the composition as a coating on one or more of the cosmetic powder ingredients that constitute the cosmetic powder component of the lipstick composition. Indeed, in a preferred embodiment, iron oxides colorant is coated onto mica and/or bismuth oxychloride.

Yet another preferred component of the stick shaped lipstick composition is at least one antioxidant. Preferred antioxidants include BHA and ascorbyl palmitate, defined in the CTFA Cosmetic Ingredient Dictionary, Third Edition, and Vitamin E acetate, a cosmetically acceptable ingredient which will be included in the next edition of the CTFA Cosmetic Ingredient Dictionary.

The antioxidant component, which is included to bar deterioration of the lipstick composition by oxidation, when present in the stick lipstick composition, represents between about 0.05% and about 0.5% by weight of the total weight of the composition. More preferably, the antioxidant component constitutes between about 0.1% and about 0.2% by weight of the composition.

Still another preferred component of the lipstick composition is the preservative component. The preservative component, provided by one or more of the below mentioned ingredients, defined in the CTFA Cosmetic Ingredient Dictionary, Third Edition, insures that the lipstick composition will be free of microorgan-

ism infestation. Ingredients that provide this preservative function include methylparaben, ethylparaben, propylparaben, butylparaben and mixtures thereof.

The preservative component, when present, is included in a weight concentration in the range of between about 0.05% and about 1%, more preferably, between about 0.1% and about 0.6%, said percentages being by weight, based on the total weight of the lipstick composition.

A final preferred ingredient is one or more fragrances. The fragrance component provides the lipstick composition with the desired taste and aroma commonly provided by lipstick compositions. The fragrance component, because of the wide range of possible ingredients having stronger or weaker aromas, may vary in a concentration range, when present, of from about 0.01% to about 2% by weight. More preferably, 0.1% to about 1.25% by weight, based on the total weight of the composition, is fragrance.

The stick shaped lipstick composition is preferably formulated by combining various components in subcompositions which are then combined to produce the composition of the present invention.

The first such subcomposition is prepared by homogeneously melt blending together, at a temperature in the range of between about 80° C. and about 90° C., the wax component, the low viscosity ester component, the plasticizing agent component, preservatives and antioxidants and a fraction of the high viscosity surface oil component.

The second subcomposition, if present, comprises the fraction of the high viscosity surface oil component not added in the first subcomposition.

The third subcomposition comprises a fraction of the cosmetic powder component and, if present, the colorant agent component, which are combined in a homogeneous mixture.

The fourth subcomposition includes the remainder of the cosmetic powder component and, if preferably present, the spherical silica component. The fourth subcomposition is combined into a homogeneous solid admixture.

Finally, the fifth subcomposition is present if the lipstick composition includes a fragrance component. The fifth subcomposition constitutes the fragrance component.

In the formation of the lipstick composition the second and third subcompositions are homogeneously admixed, preferably by means of a roller mill, and added, under agitation, to the first subcomposition. The resultant composition is melt blended to form a molten homogeneous mixture. This molten mixture is blended with the fourth subcomposition to produce a fragrance-free intimately mixed composition. If a fragrance is included, it, constituting the fifth subcomposition, is blended with the molten admixture of the first four subcompositions to produce the final lipstick composition.

A preferred stick shaped lipstick composition, made in accordance with the above procedure, employing preferred ingredients discussed above, includes between about 31% and about 35% cosmetic powders, which include mica, lecithin, bismuth oxychloride coated mica and bentonite; between about 19% and about 23% low viscosity liquid carboxylic acid esters including isotridecyl isononanoate and PEG-4 diheptanoate; between about 15% and about 19% high viscosity surface oil including lanolin, castor oil, sorbitan sesquioleate and

triisocetyl citrate; between about 9% and about 13% plasticizing agents including a mixture of acetylated lanolin alcohol and cetyl citrate; between about 1% and about 3% spherical silica; between about 10% and about 14% waxes including carnauba, ceresin and PEG-20 sorbitan beeswax; between about 1% and about 10% pigment including D&C Red No. 6 barium lake and D&C Red No. 7 calcium lake; between about 0.05% and about 0.15% antioxidant including BHA; between about 0.2% and about 0.6% preservative including methylparaben and propylparaben; and between about 0.1% and about 0.5% fragrance. It is emphasized that all the percentages recited above are by weight, based on the total weight of the composition.

The following example is given to illustrate the present invention. Because this example is provided for illustrative purposes only, the scope of the present invention should not be limited thereto.

EXAMPLE

Preparation of a Stick Shaped Lipstick Composition

A lipstick composition was prepared by melt blending together in a suitable container, provided with agitation and heating means, the following constituents in the recited number of parts by weight to produce a first subcomposition.

Ingredient	Parts by Wt.
Carnauba	1.5
Ceresin	10.0
PEG-20 sorbitan beeswax	1.0
Acetylated lanolin alcohol	2.0
Cetyl acetate	9.0
Isotridecyl isononanoate	7.5
PEG-4 diheptanoate	13.0
Triisocetyl citrate	6.0
Lanolin	1.0
Castor oil	2.7
Methylparaben	0.3
Propylparaben	0.1
BHA	0.1

A second subcomposition was prepared by blending together, in a separate container, 1.0 part by weight sorbitan sesquioleate and 7.5 parts by weight castor oil. This subcomposition was, in turn, blended with a third subcomposition formed by mixing together the pigment coloring agents, 1.2 parts by weight D&C Red No. 6 barium lake and 0.6 part by weight D&C Red No. 7 calcium lake, with 0.25 part by weight bentonite. The resultant blend of the second and third subcompositions was introduced into the vessel containing the molten mixture of the first subcomposition.

A fourth subcomposition comprising 1.75 parts by weight spherical silica; 31.0 parts by weight mica and 2.2 parts by lecithin treated mica was prepared by dry blending. This solid blend, the fourth subcomposition, was added to the contents of the vessel containing the molten mixture of the first three subcompositions and mixed until a homogeneous mixture of the four subcompositions was obtained.

Finally, 0.3 part by weight of a fragrance was added to the result subcomposition to produce the final composition.

The final composition was molded into a stick lipstick.

The above preferred embodiments and examples are given to illustrate the scope and spirit of the present invention. These embodiments and examples will make

apparent, to those skilled in the art, other embodiments and examples. These other embodiments and examples are within the contemplation of the present invention. Therefore, the present invention should be limited only by the appended claims.

What is claimed is:

1. An anhydrous stick shaped lip cosmetic composition consisting essentially of between about 15% and about 80% of at least one cosmetic powder selected from the group consisting of mica, talc, bismuth oxychloride, bentonite, nylon, silica, acrylates copolymer, teflon, spherical silica, and mixtures thereof; between about 10% and about 65% of at least one low viscosity liquid carboxylic acid ester having a viscosity of 5 to 100 cp at 25° C. and selected from the group consisting of isotridecyl isononanoate, isostearyl neopentanoate, cetyl octanoate, glyceryl trioctanoate, isodecyl oleate, isodecyl neopentanoate, PEG-4 diheptanoate, tridecyl neopentanoate, isohexyl neopentanoate, tridecyl octanoate, and mixtures thereof; between about 1% and about 18% of at least one high viscosity surface oil having a viscosity of 200 to 250,000 cp at 25° C. selected from the group consisting of castor oil, lanolin, sorbitan sesquioleate, triisocetyl citrate, and mixtures thereof; and between about 2% and about 15% of at least one plasticizing agent selected from the group consisting of acetylated lanolin alcohol, cetyl acetate, caprylic/capric triglyceride, oleyl alcohol, lanolin alcohol, octyldodecanol, or mixtures thereof; between about 5% and about 20% of a wax selected from the group consisting of carnauba, ceresin, PEG-20 sorbitan beeswax, paraffin, microcrystalline wax, glyceryl tribehenate, candelilla wax, and mixtures thereof; a pigment, antioxidant, preservative, and fragrance.
2. A composition in accordance with claim 1 wherein said cosmetic powder is coated with a hydrophobic agent selected from the group consisting of 6-aminocaproic acid, lecithin, cyclomethicone, mineral oil, or mixtures thereof.
3. A composition in accordance with claim 1 wherein the spherical silica is of particle size 1-20 microns and is present in an amount of 0.5-20%.
4. An anhydrous stick shaped lip cosmetic composition consisting essentially of between about 25% and about 45% of a cosmetic powder selected from the group consisting of mica, talc, bismuth oxychloride, bentonite, nylon, silica, acrylates copolymer, teflon and mixtures thereof; between about 25% and about 45% of a liquid carboxylic acid ester selected from the group consisting of isotridecyl isononanoate, isostearyl neopentanoate, cetyl octanoate, glyceryl trioctanoate, isodecyl oleate, isodecyl neopentanoate, PEG-4 diheptanoate, tridecyl neopentanoate, isohexyl neopentanoate, tridecyl octanoate and mixtures thereof; between about 3% and about 10% of a surface oil selected from the group consisting of castor oil, lanolin, sorbitan sesquioleate, triisocetyl citrate, and mixtures thereof; and between about 5% and about 12% of a plasticizing agent selected from the group consisting of a mixture of acetylated lanolin alcohol and cetyl acetate,

caprylic/capric triglyceride, oleyl alcohol, lanolin alcohol, octyldodecanol and mixtures thereof, between about 5% and about 20% wax selected from the group consisting of carnauba, ceresin, PEG-20 sorbitan beeswax, paraffin, microcrystalline wax, glyceryl tribehenate, candelilla wax, and mixtures thereof and a pigment, fragrance, antioxidant, and preservative; all said percentages being by weight, based on the total weight of said composition.

5. A composition in accordance with claim 4 comprising between about 0.5% and about 20% of spherical silica having an average particle size in the range of between about 1 micron and about 20 microns.

6. A composition in accordance with claim 5 wherein said spherical silica is present in a concentration of between about 1% and about 10% and has an average particle size of between about 3 microns and about 15 microns.

7. A composition in accordance with claim 4 comprising between about 1% and about 7% of pigments selected from the group consisting of iron oxides, D&C Red No. 7 calcium lake, D&C Red No. 6 barium lake, D&C Red No. 27 aluminum lake, D&C Red No. 33 25

aluminum lake, D&C Red No. 30 lake, FD&C Yellow No. 6 aluminum lake, FD&C Blue No. 1 aluminum lake, D&C Orange No. 5, D&C Red No. 21, D&C Red No. 27 and mixtures thereof.

8. A composition in accordance with claim 7 comprising between about 0.1% and about 0.2% of an antioxidant selected from the group consisting of butylated hydroxy anisole, ascorbyl palmitate and Vitamin E acetate.

9. A composition in accordance with claim 8 comprising between about 0.1% and about 0.6% of a preservative selected from the group consisting of methylparaben, ethylparaben, propylparaben, butylparaben and mixtures thereof.

10. A composition in accordance with claim 9 comprising between about 0.1% and about 1.25% of a fragrance.

11. A composition in accordance with claim 4 wherein said cosmetic powder is coated with a hydrophobic agent selected from the group consisting of 6 aminocaproic acid, lecithin, and a mixture of cyclomethicone and mineral oil, said hydrophobic agent coating representing between about 1% and about 5% by weight of said hydrophobic coated cosmetic powder.

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US005356617A

United States Patent [19]
Schlossman[11] **Patent Number:** **5,356,617**
[45] **Date of Patent:** **Oct. 18, 1994**[54] **PIGMENT-MATERIAL-MICROSPHERE
COMPLEXES AND THEIR PRODUCTION**

- [75] **Inventor:** David S. Schlossman, W. Orange,
N.J.
- [73] **Assignee:** Kobo Products, Inc., South Plainfield,
N.J.
- [21] **Appl. No.:** 986,260
- [22] **Filed:** Dec. 7, 1992

Related U.S. Application Data

- [63] Continuation-in-part of Ser. No. 523,315, May 14,
1990, Pat. No. 5,314,683.
- [51] **Int. Cl.³** A61K 7/021; A61K 7/035
- [52] **U.S. Cl.** 424/63; 424/64;
424/69; 424/78.03; 424/401; 428/403; 428/404;
514/770; 514/772.3; 514/844
- [58] **Field of Search** 424/490, 63, 64, 401
- [56] **References Cited**

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4,756,906 7/1988 Sweeny 424/63

Primary Examiner—Thurman K. Page
Assistant Examiner—James M. Spear
Attorney, Agent, or Firm—Handal & Morofsky

[57] **ABSTRACT**

New cosmetic raw materials are provided in the form of complexes of pigment materials coupled to small microspheres providing complexes that impart richness and feel, with low oil absorbency while displaying the optical and other properties of the pigment. Improvements in spatial disposition of small pigment particles provide a better dispersion of pigment in and products such as makeups, creams, lipsticks, blushers, nail enamels, and the like. Preferred embodiments include talc, nylon, silica, starches and iron oxide pigments coupled by a liquid titanate coupling agent to microspheres of polyvinylidene chloride copolymer, polyethylene, nylon and silica. Simple methods of manufacture include spraying a liquid titanate in solution on a blended mixture of pigment and microsphere and drying the product while blending, to cure it.

20 Claims, 9 Drawing Sheets

FIG. 2

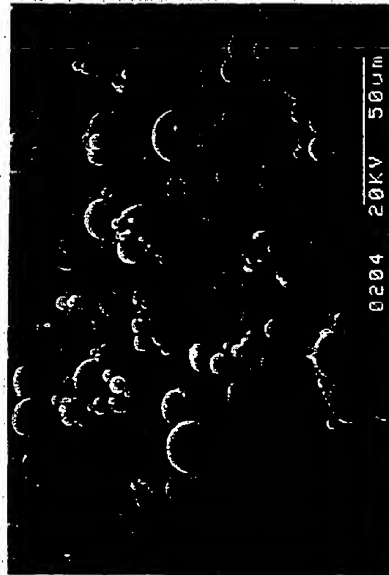


FIG. 1

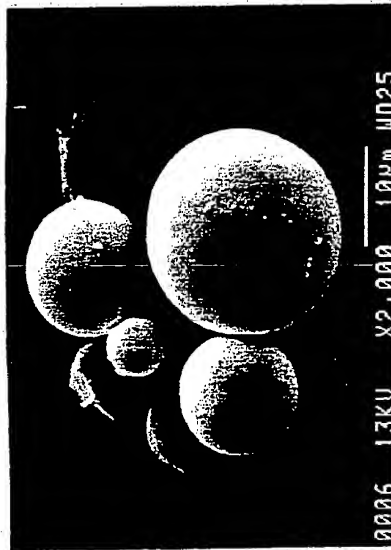
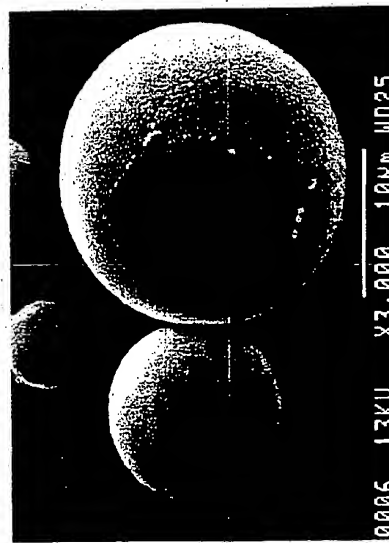


FIG. 4



FIG. 3



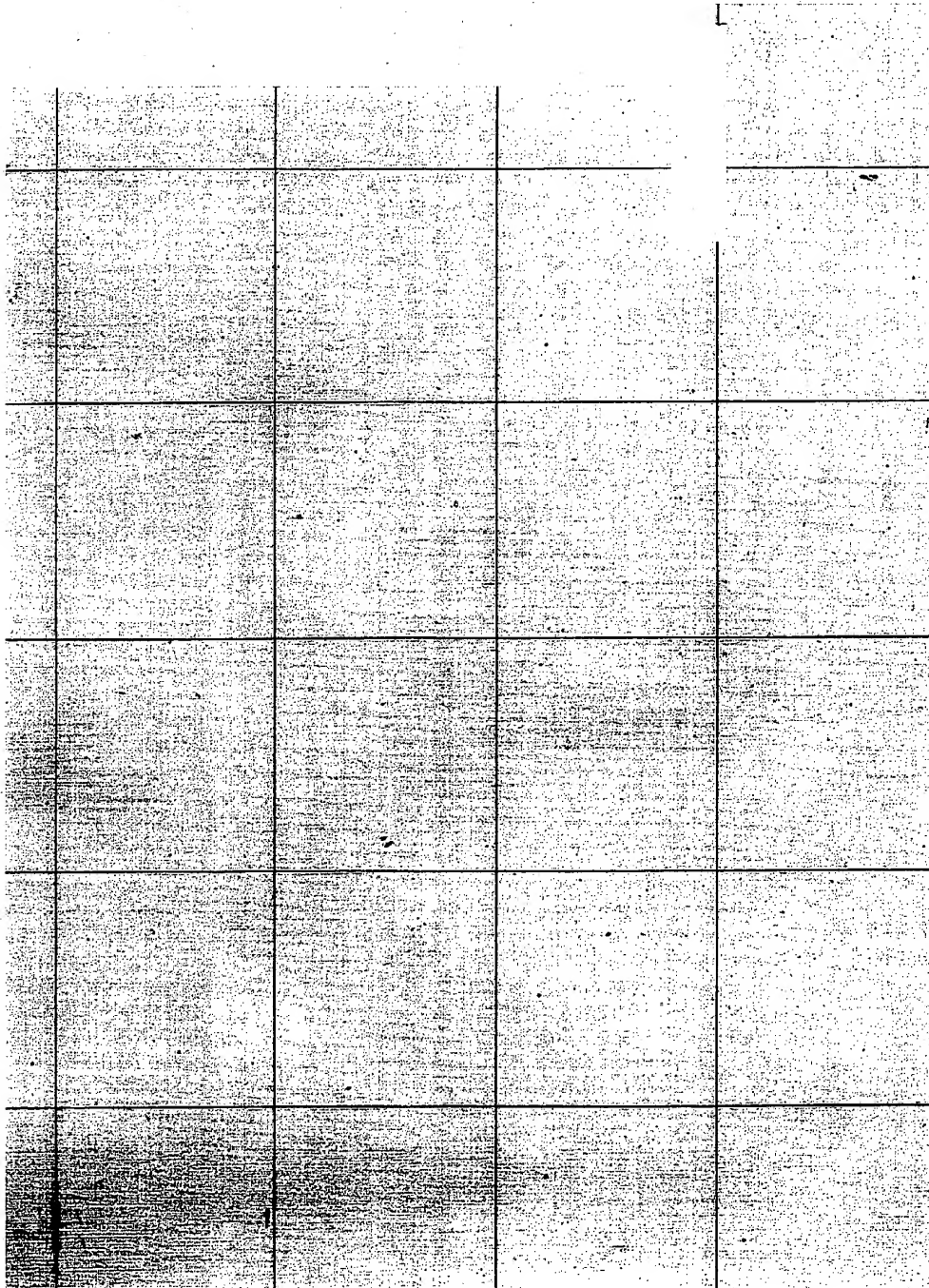


FIG. 9

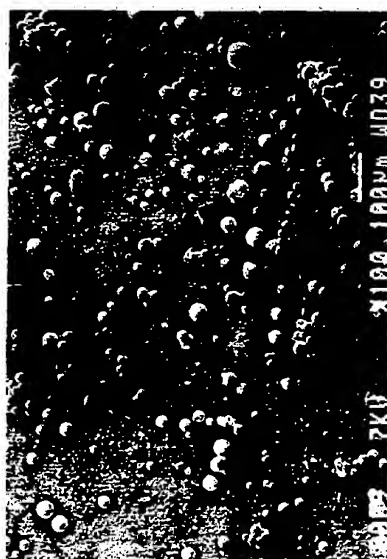


FIG. 10

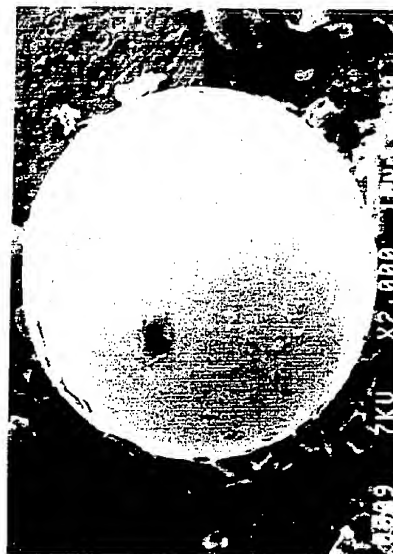


FIG. 11

FIG. 13



FIG. 15



FIG. 12

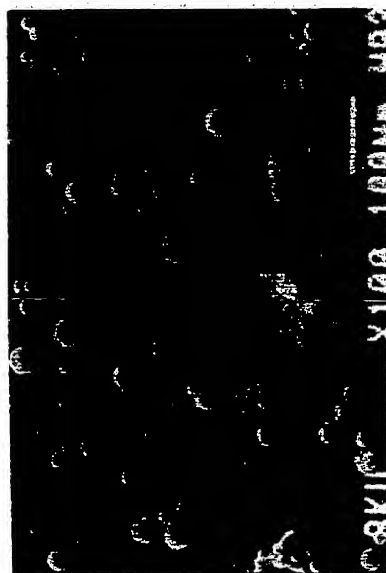


FIG. 14



FIG. 16

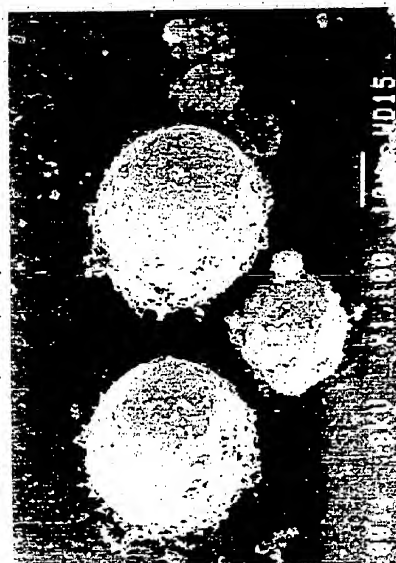
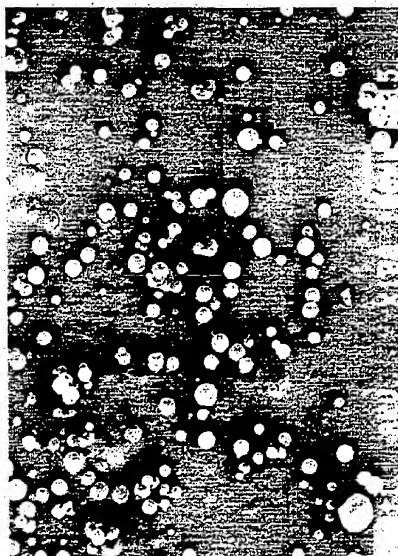


FIG. 17



FIG. 18

FIG. 19

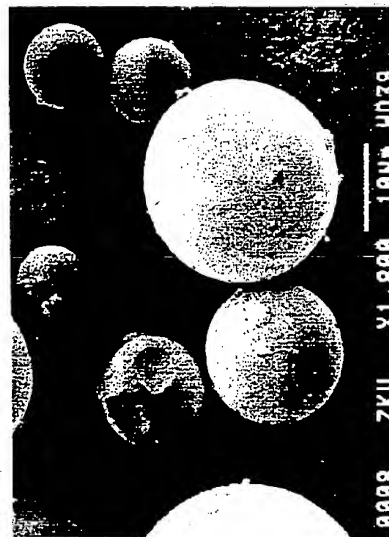
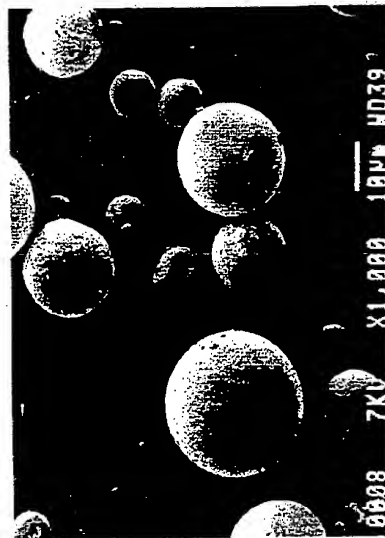


FIG. 20

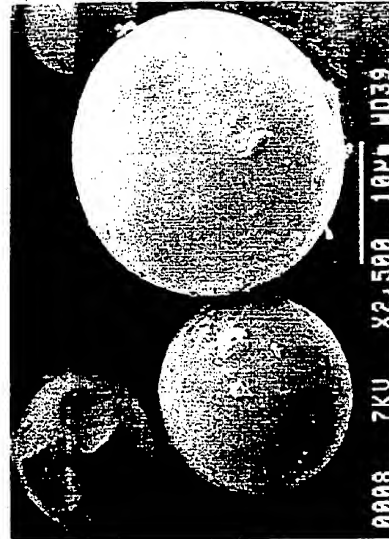


FIG. 21

FIG. 22



FIG. 23



FIG. 24



FIG. 25

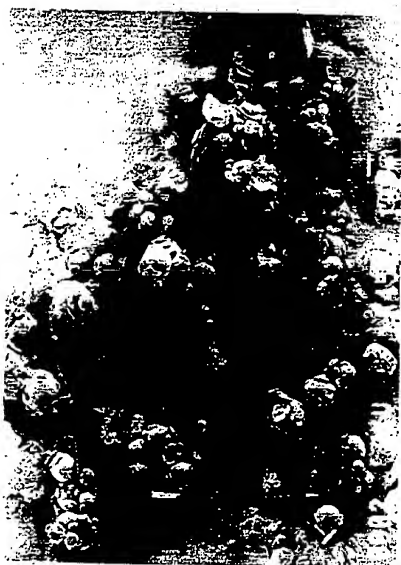


FIG. 26



FIG. 27

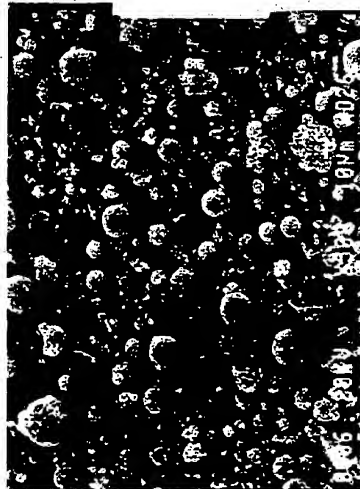


FIG. 28



FIG. 29

PIGMENT-MATERIAL-MICROSPHERE COMPLEXES AND THEIR PRODUCTION

CROSS-REFERENCE TO A RELATED APPLICATION

This application is a continuation-in-part of my co-pending U.S. patent application Ser. No. 07/523,315, filed May 14, 1990 now U.S. Pat. No. 5,314,683 and entitled "Method of Coupling Cosmetic Materials and Cosmetics Containing Coupled Materials".

TECHNICAL FIELD

The present invention relates to new cosmetic raw materials in the form of novel complexes of microspheres with cosmetic materials and the manufacture of such raw materials. The new complexes impart unique and desirable characteristics to cosmetic end-product formulations in which they are employed as ingredients. The invention can utilize either organic or inorganic microspheres.

BACKGROUND

Since prehistoric times, when body paint was first being applied, separation of pigments and other components in paints and dyes has led to inconsistent colors and non-uniform applications of make-up. Separation and settling is a well-known phenomenon in liquid, or fluid-phase systems, that results in diminished shelf-life, non-uniform colors and ineffectual application of make-up. Separation can also take place in powder mixtures with the less dense material tending to concentrate in the upper volume of the mixture.

Advances in the cosmetic arts, and the choice of possible cosmetic formulators, are constrained and limited by, among others, the following requirements:

- compatibility, both physical and chemical, with customary cosmetic formulators and pre-cursor materials which can include both hydrophilic and lipophilic materials;

- stability, again both physical and chemical and also biological, in end-product formulations for extended distribution and shelf-life, especially against settling, loss of volume and spoilage;

- end-product stability for the consumer after opening;
- end-use functionality which, in addition to the more or less subtle ornamental functions required of, for example, lipstick, mascara, face powder and nail polish, includes the more elusive qualities of feel, ease of application as well as an appropriate range of adhesion; and, most importantly,

- non-toxicity, non-comedogenicity, hypoallergenicity and the like, in other words, dermatological innocuity.

Many, but not all, of these properties can be related to dispersibility of the pigment materials and the art is replete with proposals for improving pigment dispersibility. Noting that a pigment can be considered as a concentrated particle of colorant or other material providing a useful visual effect, including pigment extending, techniques to improve dispersibility usually comprise grinding or milling pigment materials to a fine particle size and coating the particles.

Milling of course increases the available surface area and visual effect of the pigment, and thus its effectiveness. There are many prior art teachings relating to the coating of pigment materials to improve their dispersibility. Most pigment materials tend to have a hydro-

philic surface character making them hard to disperse in organic media, and it is accordingly well-known to treat pigment materials to give them a hydrophobic character and to use surfactants, anti-flocculants and the like to improve the dispersibility of the pigment materials.

The present invention takes a new approach to the improvement of dispersibility, providing striking results of great value to the cosmetics industry. Indeed the invention succeeds in providing some control over the spatial distribution of particulate pigment materials in subsequent cosmetic formulations.

In U.S. Pat. No. 4,877,604 to M. Schlossman there are described a number of methods to coat pigments and pigment materials with titanate coupling agents including isopropyl triisostearoyl titanate. M. Schlossman provides valuable improvements in the art of pigment material dispersibility.

In a different industry, with different constraints, the plastics industry, materials known as spherical polymeric particulates in powder form and hollow spheres in powder form, either of which materials may be called microspheres, are known as valuable fillers and are prized for their sphericity, controlled particle size and low density, see for example, Ruhno "Handbook of fillers for plastics", edited by H. S. Katz et al, pp. 437-438 Van Nostrand Reinhold (1978).

According to Ruhno, there are major advantages to the plastics industry in the ability of microspheres to act as fillers in composite materials, displacing high-priced polymers with lower density, and better density control than solid mineral fillers. Some end product advantages are uniform shrinkage, improved sandability and increased impact resistance.

A brief review of the history and development of spherical polymeric powders or microspheres, including hollow spheres, sized under 1000 micron, can be found in the Ruhno reference. Inorganic and organic hollow spheres are described and referred to as "microspheres" the term being used for materials which are spherical, small and light, and in the context of this reference, hollow and polymeric. Obviously, the above-described end-product advantages are not of general use in cosmetics.

Native organic polymeric microspheres have been incorporated in cosmetic compositions to impart desirable texture characteristics of smoothness and feel, as well as pourability to powder cosmetics, notably makeup, see for example UK Patent Application GB 2 191 945. An important drawback is high oil absorption causing excessive drying and caking. Another problem is that small round microspheres do not adhere well to the skin.

Inert microspherical materials, especially organic polymeric materials, for example spherical nylon or polyethylene powder, have been employed as a cosmetic raw material, see for example, the Journal of The Society of Cosmetic Chemists, 41, 197-207, May/June 1990 ("Cosm. Chem." hereinafter). Here, hybridized powders are disclosed in which fine-chemical deodorant powders, specifically zinc oxide and aluminum chlorhydrate are mechanically layered on such microspheres by mixing and percussion in a centrifugal ball mill. The active, chemical quenching power of the deodorants is retained and improved physical properties of the deodorant powders result, including better texture and lower coefficients of kinetic friction, the latter correlating with smoothness.

Mechanofusion processes are expensive and difficult to use on a commercial scale for bulk raw materials. A drawback of such cosmetics-containing microspherical particles produced by mechanofusion processes, especially organic polymeric particles, is that they can have too high an oil absorption capacity, giving an unacceptable drying effect to the skin. Furthermore, the mechanical layering technique results in the outer powders being partially buried, reducing their exposed surface area, a drawback for pigment materials. Another difficulty may arise during pulverization when too much heat can cause polymeric microspheres to melt.

Also, while deodorants may be embraced by some interpretations of the term "cosmetic" their properties are obviously not those required for decorative cosmetics as a material used to adorn embellish or beautify the wearer, to enhance the visible appearance of exposed surfaces of the wearer, and they are not usually applied to normally exposed skin surfaces.

The Cosm. Chem. disclosure is silent as to the suitability of small inert spherical powders for inclusion in appearance-enhancing cosmetics, especially for topical application where the oil absorption and light-reflective properties of cosmetics are paramount. Nor is the Cosm. Chem. disclosure relevant to liquid phase dispersions for manual application by spreading. Certain additional properties are vital for appearance-enhancing cosmetics. These properties include not only their appearance and their ability to sustain and develop pigments, but also end-product characteristics such as spreadability.

Additionally, while the physical properties of feel and smoothness that can be contributed by microspheres in some formulations may be desirable out of the container, these are of no value if the product lacks adequate adhesion to remain on the skin. This is a further drawback of microspheres.

Broad usage of microspheres is contraindicated by high cost in addition to technical factors. Formulators may encounter difficulties during processing, for example, blending inconsistencies arising from bulk density differences; pressing problems in which oil can come out, and stability problems because prolonged oil absorption can cause dried cake, cracking, and impair the texture of the product. In addition, smooth, round particles do not adhere well to the skin.

SUMMARY OF THE INVENTION

This invention solves a problem. One of the problems it solves is the provision of an improved pigment material which is readily dispersible in cosmetic compositions and which has improved bulk density and specific surface area characteristics.

Another object of the invention is to provide a new class of cosmetics having richer, more luxurious qualities than have heretofore been obtainable.

It is a further object of this invention to provide improved pigment materials having excellent dispersibility which materials are notable for comprising a wide class of both inorganic and organic pigments pigment extenders and other special, visual-effects materials, and are also notable for enhancing the cosmetic properties of these pigments and pigment materials.

A still further object of the invention relates to providing an improved cosmetic material which enables microspherical powders to be employed in decorative cosmetics without being subject to the drawbacks of known materials.

Additional objects relate to the provision of improved processes for formulating cosmetics and to novel processes for the manufacture of the novel cosmetic ingredient materials of this invention.

Broadly stated, the invention provides novel pigment-material complexes for use in commercial formulations, especially cosmetics, in which a particulate pigment material is chemically coupled to a microsphere material. To simplify the coupling reaction and reduce possible chaining or polymerization, where the pigment material is inorganic, polar or hydrophilic, an organic, non-polar hydrophobic and preferably polymeric microsphere material is used as a carrier for the pigment material. Similarly, hydrophobic organic materials are preferably coupled to inorganic microparticulate carriers, for example by hydroxyl groups on adsorbed water molecules.

However, "homo" complexes in which microspheres are cross-linked are also contemplated as being useful embodiments of the present invention, for example nylon-nylon complexes or silica-silica complexes.

Preferably, the pigment material size is less than that of the microspheres, nearly all the particles of which should have diameters less than 1000 microns, and a number of pigment particles is coupled to each microspherical particle to create what can be thought of as a pincushion effect in which a plurality of smaller pigment particles is chemically bonded or tethered to the surface of a microsphere in a manner providing general coverage of the surface of the microsphere with the pigment particles distributed in a shell-like zone close to the surface of the microsphere particle to which they are attached, like the heads of pins sticking out of a pin cushion. This novel material can be described as a pigment-material-microsphere complex and is an excellent raw material for use in ornamental cosmetics.

In one aspect, the invention provides an improved hydrophobic, dispersible, high-loading cosmetic material with a low surface area-to-volume ratio, low bulk density comprising a pulverized inorganic cosmetic pigment material coating and coupled to from 5 to 35 percent of an organic polymeric microspherical powder of diameter less than 1000 microns by from 1 to 5 percent of a titanate coupling agent wherein the inorganic pigment material is smaller than the organic microspheres and the coupled product has a generally spherical particulate shape, said inorganic cosmetic material and said cosmetic material being capable of being coupled by said titanate coupling agent.

In another aspect the invention provides an pigment-material-microsphere complex of low specific density comprising:

- a) microsphere-material particles having a particle size less than 1000 microns;
- b) a plurality of pigment-material particles covalently bonded to said polymeric particles; and
- c) a coupling agent residue extending between said pigment materials and said microsphere particles whereby they are covalently bonded;

one of said microsphere or said pigment materials being an organic material and the other being inorganic and said coupling agent residue being derived from a coupling agent reactive with said microsphere particles and reactive with said pigment material particles.

While some ionic attraction or van der Waal's bonding may be a component of the chemical bonds providing the coupling, it is preferred for the coupling to be by covalent bonding, or electron sharing.

A particularly desirable complex has a substantially uniform layer of pigment particles coupled to each microsphere so as fully to coat it and present the pigment's visual properties more or less substantially uniformly in all directions from the complex particle, in the manner of an outer skin.

Such inventive complexes are useful when incorporated in liquid phase or semi-solid dispersions for manual application by spreading, including make-up, nail enamel eye shadow and the like. The complexes can impart valuable additional properties to appearance-enhancing cosmetics. These properties include not only good appearance and ability to sustain and develop pigments, but also end-product characteristics such as spreadability. Additionally, the novel cosmetic-material complexes of this invention can provide valuable processing advantages in the manufacture of such cosmetic end products, and the invention extends to such improved manufacturing process which use microsphere-complexed pigment materials in place of conventional pigments and the invention further relates to the new cosmetic end-products that result.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In a preferred embodiment, the invention relates to novel complexes of discrete, particulate cosmetic materials, especially irregularly shaped materials, such as pigments and what may be called pigment materials, which term is often used to include pigment extenders and other materials that modify the characteristics, especially the visual characteristics, of the end product cosmetic, for example, talc, silica, sericites and pearlcents and mica.

Pigments coupled according to the invention are held in a novel spatial distribution which avoids agglomeration and reduces settling and furthermore facilitates dispersion in hydrophobic media. The resultant approximately spherical single-particle layers exhibited by preferred embodiments of the invention provide a very efficient spatial distribution of the pigment with good fill in formulations and excellent display of the pigment's visual properties.

The novel complexed pigment materials of this invention are valuable ingredients when substituted for standard pigments in many cosmetic formulations, to which they bring richness, smoothness and other desirable properties. Of particular interest are: powder make-up compositions, where controlled oil absorption is important so that the make-up does not dry the skin; and aqueous or oil-phase cosmetics where the improved dispersibility of the pigment complexes is valuable.

In a liquid system, improved dispersion may be achieved through reduction of surface area of the material being dispersed, i.e., spherical particles disperse more uniformly than cubic or irregular shaped particles. Improved dispersion also allows higher levels of pigment material to be loaded into the dispersant.

Many diverse coupling agents can be used to provide a bond between the pigment material and the microsphere material. The coupling agent must be capable of bonding. So both the pigment material and the microspheres under reaction conditions that will not be deleterious to either ingredient. Preferably, the coupling agent has one functional group that is reactive with the pigment material and a different group that is reactive with the microsphere material. The residual linking group should be inactive or innocuous in cosmetic com-

positions and in their processing. Preferably also, the coupling agent coats the pigment material to improve its dispersibility without unduly detracting from its pigmenting properties.

In general, organofunctional coupling agents are preferred, especially those with a hydrolyzable moiety that will couple to an inorganic material and a non-hydrolyzable moiety that will couple to an organic material. While the parameters of suitable coupling agents will be discussed more fully below, many suitable agents can be found in the various chemical arts and they include classes of compounds such for example as of organofunctional aluminates, titanates and zirconates as well as organofunctional silanes.

A preferred class of coupling agents comprises titanate coupling agents, and these are effective in coating inorganic pigment materials, giving them a hydrophobic character rendering them more compatible with oily phase dispersants.

The invention relates to the coupling of particulate components of a make-up. An organic particulate material can be coupled with an inorganic particulate material to provide a combination or complex that is a homogeneous, uniform material that resists separation and disperses better than an uncoupled mixture of the same materials.

Microspheres are value-added ingredients in today's formulations. In a preferred embodiment, the invention extends and adapts some of the desirable properties of microspheres to irregularly shaped organic and inorganic pigments, using an isopropyl triisostearoyl titanate to couple pigment materials to microspheres. The new complexed compounds of this invention offer increased applications not achievable by the uncoupled components whether used singly or together.

Microspheres disperse more uniformly than most pigments in both oil and aqueous-based systems and also in emulsions, having the lowest specific surface area per unit volume. Produced to a narrow particle size range, microsphere complexes blend more uniformly in pressed and loose powder systems. The pigment-complexed microsphere materials of this invention have many of these advantages while, depending upon the particular pigment and microsphere material chosen, avoiding many of the drawbacks of employing microsphere materials, especially organic polymeric microsphere materials in cosmetic compositions.

The inventive cosmetic pigment-material-microsphere complexes have markedly improved and useful characteristics for cosmetics including: a low surface area to volume ratio; improved dispersion; improved viscosity and better flow; and uniform reflectivity.

Commercially available microspherical powders useful in the preparation of the cosmetic materials of this invention include organic polymeric materials such as polyethylene, polypropylene and copolymers thereof, polyurethane, polyesters, polyamides, polymethylmethacrylate, nylon, ethylene acrylates copolymers and polyvinylidene copolymers. Substantially any non-toxic, non-irritant, cosmetically compatible organic polymeric material that can be satisfactorily coupled, can be used. Inorganic microsphere powders including, for example, silica, magnesium carbonate, and titanium dioxide can also be used.

Both organic and inorganic microspheres can be solid, porous or hollow or mixtures thereof. Such microspherical powders generally have diameters of less than 1000 microns and preferred powders have diame-

ters of from 1 to 100 microns. Effective results can be obtained with microspheres of from 2 to 50 microns with many useful, commercially available microsphere materials falling in the range of from 2 to 20 microns. Although useful results can be obtained with microspheres having an average size of about 2 microns, larger diameters for better spatial distribution of coupled pigments are preferred.

The characteristics of some commercially available microspherical powders useful in the practice of this invention are set forth in Tables:

TABLE 1

Typical Values of Quantitative Microsphere Properties.				
	Avg. Particle Size microns	Apparent Density g/in ³	Oil Absorption g/100 g	Melting Point °C.
Ethylene Acrylates Copolymer	5-15	2.4	60	104
Polyethylene	10 ± 2	2.9	90	109
Nylon I	5	3.9	55	165-171
Nylon II	2-20	—	90	—
Polymethylmethacrylate (PMMA)	2-15	5.4	60	N/A
Silica	9 ± 2	5.5	150	N/A
Polyvinylidene copolymer (PVDC)	5-35	0.2	1270	N/A
Polyurethane	10	8.3	60	N/A

Apparent density is determined on the loose material. Oil absorption is determined by ASTM D281-84. "N/A" is "not applicable".

1 An example of a suitable class of polyvinylidene copolymers is that of acrylonitrile vinylidene chloride copolymers.

TABLE 2

Qualitative Microsphere Properties					
	Organic	Inorganic	Solid	Hollow	Porous
Ethylene Acrylates Copolymer	X		X		
Polyethylene	X		X		
Nylon	X		X		
PMMA	X		X		
Silica		X			X
PVDC	X			X	
Polyurethane	X		X		

Of particular interest is the PVDC material listed above which comprises hollow microsphere particles and has an exceptionally low apparent or bulk density. Such materials, when complexed according to the methods of this invention, provide a particularly attractive product whose low density imparts a highly desirable bulk density reduction to pigment materials with which they are complexed. Further advantages are desirable characteristics such as richness and smoothness in cosmetic formulations and also high oil-absorption characteristics to the cosmetic. (As noted above, the oil absorption of raw, hollow polymeric microspheres may be excessive.) Hollow microsphere forms of other organic polymers are available and similarly advantageous. Bulk densities below 0.5 g/in³ are available and useful. Such materials are extremely hard to process in their raw state as they become airborne and fly everywhere. Complexing by the method of this invention solves this problem.

Preferred embodiments of the cosmetic materials include pigment materials, both inorganic materials, especially those that are customarily ground before use and also inorganic materials that are sometimes irregularly shaped, in the sense that they are clearly not spherical, are prone to have notably angular surfaces with

occlusions and voids between particles and tend to include a wide range of particle sizes within samples. Such features are characteristic of many inorganic pigment materials. Organic pigments tend to be gritty, having sharp angular surfaces. Being small relatively high density particles, they are hard to disperse and to keep in suspension.

Some examples of irregularly shaped organic and inorganic pigment materials that can be used as particulate cosmetic materials to be coupled to microspheres are: boron nitride, D&C red #6 barium lake, D&C Red #7 calcium lake, D&C red #34, FD&C blue #1 aluminum lake, yellow, black and red iron oxide, carmine, ferric ammonium ferrocyanide, ferric ferrocyanide, manganese violet, ultramarine blue, ultramarine violet, ultramarine pin, silica, mica, talc, bismuth oxychloride, titanium dioxide, nylon, flour, starch, complexed metal starches and polyethylene, and metallic powders, including for example, aluminum powder and bronze powder. Clearly such metallic powders will require a choice of process conditions that attaches to the surface of the particles and avoids destroying the body of the particle itself. Pigment materials generally range in size from about 15 nanometers to 10 microns, with coloring pigments not usually exceeding about 2 microns in approximate diameter.

While the lower limit may appear to be extremely small, it should be noted that a commercially available titanium dioxide pigment has an average primary particle size of 21 nm and a specific surface area of about 50m²/g and there are common pigments, such as iron oxide pigments that are known to be smaller. It can readily be appreciated that a substantially continuous shell of such fine-particulate pigment coupled to an organic microsphere of several microns diameter achieves an excellent spatial distribution of the pigment with much improved covering power and apparent bulk density, a quite new material.

In making the present invention, I have discovered that by coupling irregularly shaped or multi-faceted pigment materials to the microspheres described above using for example titanate coupling agents, the coupled pigment products acquire many of the desirable physical characteristics of the microspherical powders while retaining their valuable pigment properties. Importantly, the basic spherical shape of the microspheres is maintained in the coupled material, so that what were in many cases small, irregularly shaped, multi-faceted pigment materials having a tendency to agglomerate are now held in an organized spaced relationship. This spacing improves many of their cosmetic characteristics, especially the coupled pigment materials' dispersibility. Clearly this improvement in dispersibility is more than mere improvements in phase compatibility obtainable by prior art surface treatments, because reductions in bulk density of the rather dense pigment materials which are provided by the present invention, help reduce any tendency of the materials to settle out.

Such irregularly shaped complexed pigment materials can be considered as being distributed around each microsphere particle on generally spherical or spheroidal surfaces or in generally spherical shells, with radii greater than the average pigment particle size, preferably at least two or three times the size. This distribution is illustrated in a general manner in the accompanying micrographs which will be described hereinafter. In this way optimal use of the surface properties of the pigment

is obtained. The complexes display similar reflectivity in all directions. In general, these complexes will be much larger in size than any of the cosmetic materials with which they are formulated and will naturally tend to present an evenly pigmented outer surface at any exposed surface. This of course is a highly desirable cosmetic characteristic. The size of the generally spherical complexes provides plenty of room for smaller particles to be accommodated between them. Their sphericity promotes blendability with other cosmetic ingredients.

A further and surprising advantage is displayed by the inventive complexes in that, where adequate pigment material is used in manufacturing the complex, the oil absorption characteristics of hydrophilic polymeric microspheres, especially very absorbent hollow ones, can be significantly reduced. This is important, to avoid undue drying effects of the end product caused by excessive absorption of skin oils.

Thus, the pigment shell or coating on a low-density, organic, polymeric microsphere particle, or core, can protect or modify the properties of that core, while gaining improved spatial distribution leading to isotropic light reflectance, bulk density and specific surface area characteristics for the pigment material. There is a synergistic relationship, the one material gaining properties from the other. Thus, the presence, especially of a hydrophilic or oleophobic pigment coating, can reduce the accessibility of an oleophilic organic core to oils, and thus control oil absorption. In this context, a shell of silica particles can greatly reduce the oil absorbency of organic polymer microspheres, especially if it is a more or less solid or closed shell. Inorganic, unreactive materials such as silica usually have a small quantity of adsorbed water providing available sites for the attachment of hydrophilic moieties.

In some cases, the microspheres may be many times the size of the pigment material, 10, 50 or even 100 times, so long as the size of the resultant pigment-material-microsphere complex particle does not exceed about 1000 micron (1 mm.)

Alterations of the microspheres' qualitative properties may also be made, yielding advantages in the resulting composition or processing of the composition. For example, they may be treated with surfactants to make them more dispersible, of value with silica, or pH-modified by an acid treatment or base-catalyst treatment.

The irregularly shaped coating or pigment materials should be ground, milled or pulverized to a size, preferably between 15 nanometers and 10 microns, in relation to the microspheres, which is such as to enable the material to coat the microspheres and provide a coupled product or complex having a generally spherical shape. Such comminution of the pigment material typically results in particles that have sharp angular faces and that are far from spherical. Organic pigments, in particular, are gritty when comminuted. Complexing with inorganic microspheres improves the bulk texture and blendability of such gritty organic pigments.

It has been discovered that a titanate coupling agent can join an inorganic material to an organic microspherical powder and join organic material to an inorganic microspherical powder. In joining the materials, moisture and air voids on the irregularly shaped material can be eliminated when these materials are coupled to the microsphere, thus tremendously reducing the surface area.

An improved method is to solubilize the titanate coupling agent in a volatile solvent such as isopropyl alcohol, heptane or, preferably, a high-purity, fractionated isoparaffinic solvent, and then mix it with or spray it on the materials to be coupled.

Liquid monalkoxy (C_1 to C_{20}) isostearoyl titanates, especially isopropyl triisostearoyl titanate, have been found effective as coupling agents in accordance with the invention.

Titanate coupling agents are well known materials and they can be used in a number of different coupling processes that are described in relevant literature, for example a chapter entitled "The Chemistry of Titanate Coupling Agents", pages 2-9 and 26-29 in "Ken-React Reference Manual—Titanate, Zirconate and Aluminate Coupling Agents", Monte et al., and M. Schlossman U.S. Pat. No. 4,877,604.

In general terms, a titanate coupling reaction mechanism is believed to proceed as follows.

A monohydrolyzable group attaches to a proton on the surface of an inorganic pigment material, followed by hydrolysis or solvolysis, and then transesterification and transalkylation, whereupon the water of hydration and air voids on the inorganic pigment surface are replaced by a monomolecular layer of organofunctional titanium, the titanate forming a covalent bond (electron sharing) with a proton on the inorganic surface. The titanium is bonded to oxygen atoms and to the inorganic surface. The coated inorganic material is then able to be joined to a microspherical surface, especially an organic surface, by the coating.

Monte et al. U.S. Pat. No. 4,098,758, the disclosure of which is herein incorporated by reference thereto, describes one class of titanate coupling agents which can be used to couple inorganic pigments to organic polymers and which have the advantage of avoiding multi-layer coatings on the pigment. These coupling agents can be used in the practice of the present invention. Furthermore, analogous titanate coupling agents having different proportions of hydrolyzable to non-hydrolyzable groups from those required by Monte, can be used. There is a great diversity of substituents that can be present on the coupling agent. Many of these are set forth in Monte. Such titanate coupling agents can also be used to couple organic pigment materials to an inorganic microsphere carrier.

Clearly other coupling agents can be used with similar effect and advantage, for example, zirconate or aluminate coupling agents such as neopentyl (diallyl) oxyl, tri(dioctyl) phosphito zirconate and equivalent aluminates. However, titanates constitute a preferred species, whose effectiveness and desirability for the purposes of this invention have been demonstrated by experiment, as disclosed herein and are known to cosmetically compatible with few, if any, undesirable side effects. The use of titanium in the form of titanium dioxide is of course a standard practice in the cosmetic arts and its safeness is well established.

A number of surfactants having a polar terminus for attachment to or coating inorganic pigments having a hydrophilic surface, such as those disclosed in Ayala U.S. Pat. No. 4,952,651, can also be used as coupling agents. These surfactant-type coupling agents include, for example, triols, especially trimethylol ethane and propane and dimethyl polysiloxanes. Ayala's surfactants have, in addition to a reactive polar terminus capable of attachment to active sites on hydrophilic pigment particles, a non-polar terminus for compatibility with a

non-polar matrix such as a polyolefin. While such agents could be used in the practice of the present invention to complex polar and non-polar particles, and can be effective for example where the polar terminus comprises an extensive alkyl or alkyl-substituted ligand that binds to polymer microspheres reasonably well by van der Waal's forces, it is preferred that the non-polar terminus be reactive and be capable of being chemically covalently bound to an organic microsphere without disturbing the bonding to the pigment.

In summary, a coupling agent for coupling polar particles having active sites to non-polar particles can have the general formula:



where M is a carrier moiety with a valency state of from 2 to 6, preferably from 2 to 4; n and m is each from 1 to 5 with n+m equaling said valency state; X is a polar-reactive ligand reactable with said active sites on said polar particles and Y is a non-polar-reactive ligand reactable with said non-polar particles.

M can be selected from the group consisting of metallo moieties including titano, zircono and aluminio, phosphato or phosphito moieties, secondary, tertiary or quaternary substituted ammonium moieties and bi-, tri- or quadri-functional organic groups, including aliphatic, cyclic, heterocyclic and polycyclic organic moieties.

X preferably includes a hydroxyl or alkoxy moiety of from one to five carbon atoms and is hydrolyzable, but other polar-binding ligands can be used.

Y can be any ligand which will couple to the desired non-polar particle, be it pigment material or microsphere without interfering with the X-bond to the polar particle. Examples of suitable Y ligands include alkoxy groups having from 1 to 24 carbon atoms, such as stearoyl, oleyl, and palmitoyl, straight, branched chain and cyclic homologues thereof, either saturated or unsaturated, and substituted homologues thereof with halo, amino or nitro substituents.

Thus, in general terms, a preferred class of coupling agents comprises a monohydrolyzable ligand for attachment to inorganic pigment materials by hydrolysis, a metallo carrier moiety and an organofunctional ligand or ligands for attachment to the organic polymeric microspheres. Conveniently, the organofunctional ligand can comprise an ester-like moiety that can attach to paraffinic chains or groups in the polymeric microspheres by trans-esterification and trans-alkylation.

Many other variants of M, X and Y that can serve the general purposes of this invention will be apparent to those skilled in the art from the disclosure herein and from the literature cited herein, as well as from other literature known to those skilled in the art. Isopropyl trisostearoyl titanate, the preferred coupling agent used herein, exemplifies the formula above. Another class of possible coupling agents, not discussed above, comprises organofunctional silanes, especially those possessing both organic and inorganic reactivity, (the possession of which is a feature of preferred coupling agents) for example, Dow Corning Z-6020 silane which is designated N-(beta-aminoethyl)-gamma-aminopropyl-trimethoxysilane of formula $(CH_3O)_3Si(CH_2)_3NH(CH_2)_2NH_2$. Notable are the aminoalkyl organic group and the trimethoxy silyl inorganic group which can serve as coupling moieties in a variety of coupling agents. Other usable silanes include amine,

epoxy, vinyl, chloralkylamine and vinylbenzylamine homologs of the above Z-6020 silane.

Preferably, the coupling agent is chosen to favor the coupling of a number of pigment particles to a single microsphere without chaining or layering of the coupling agent. Depending upon their relative particle sizes, this number is preferably at least four and even at the outer limits of relative proportions is probably not in excess of a thousand, while 100 is a more practical maximum. An optically continuous layer of pigment particles is desirable.

It is also preferred that the coupling agent be capable of coating inorganic pigment particles having a hydrophilic surface to render that surface hydrophobic and the particles dispersible. Using such a coupling agent and appropriate process conditions, a pigment-material-microsphere complex can be produced which presents hydrophobic, non-polar surfaces regardless of the character of the inorganic pigment coating the complex; which has isotropic reflectivity displaying the optical character of the pigment material; which is dispersible in oils and has desirable density and specific surface area characteristics. Isopropyl trisostearoyl titanate and other organotitanates are examples of such microsphere-coupling materials that can also coat inorganic pigment particles.

In a preferred embodiment, the organofunctional group or groups, and there can be three such groups per titanium atom, are alkoxy groups, giving the coated inorganic pigment material a hydrophobic or lipophilic surface. As disclosed and claimed by M. Schlossman, such pigment materials have improved dispersibility in cosmetic formulations and, by virtue of their titanate coating, provide surprising advantages both to the processor and the end user. These advantages perhaps can be attributed to the surface characteristics of the titanate-coated particles which, in addition to being hydrophobic, are less likely to trap air and moisture between the particles.

The present invention achieves some surprising advantages over the prior art, including M. Schlossman, by improving the spatial distribution of particulate cosmetic materials. This distribution is obtained by chemically bonding or coupling the particulate cosmetic materials to a microspherical carrier. One way of doing this is by coupling coated particles, such as those described above, to organic polymeric microspheres using per se known reaction techniques.

As a practical matter, using bifunctional coupling agents, for example organic titanates having hydrophilic and hydrophobic reactive groups, the coupling process can be effected in a single step. In such a one-step process, the particulate cosmetic material, the microspheres and the coupling agent are mixed under conditions promoting the desired coupling reactions, for example by spraying or otherwise mixing a solution of the coupling agent with a mixture of the other two ingredients, which can be a dry mix in a blender, and drying off the solvent with heat, while mixing or blending. In preferred embodiments, the coupling agent or titanate is substantially fully reacted to the particulate cosmetic material surface by the heat required to dry off the solvent.

A titanate coupling agent dissolved in an organic solvent, for example, an isopropyl trisostearoyl titanate coupling agent, will partially react at room temperature, but an elevated temperature, for example in the range of from 80° to 300° C. is preferred to effect cou-

pling. The solvent can then be removed in a drying step which usually completes the coupling reaction steps of hydrolysis, transesterification and transalkylation.

A volatile organic solvent with, for example, a distillation range between 97°-140° C., is preferred for use in the coupling process, especially where the coupling agent is a liquid monoalkoxy titanate, especially an alkyl trialkoxy titanate.

A particularly suitable solvent is an isoparaffinic solvent such as Isopar C (trade mark) manufactured by the Exxon Corporation. This has a narrow distillation range of from 98° to 106° C., has exceptional purity of isoparaffinics with low limits of other hydrocarbons and of trace impurities. Isoparaffinic solvents have similarities to heptane, which could also be used, but have a lower heat of vaporization, a mild odor and are relatively inert. Their freedom from essentially any polar compounds is of particular value in carrying out the present invention as is their low toxicity. Furthermore, Isopar C has been found to yield better coatings than other solvents, for example isopropyl alcohol.

The solvent can be added to the coupling agent or titanate to comprise between 1-99 percent of the formula. A good blend has between 5-50 percent solvent, and a preferred ratio between 15-35 percent by weight. In practicing the coupling process of this invention, the powdery ingredients, namely the particulate cosmetic or pigment material and the microspheres can be charged to a vessel provided with a vacuum system capable of removing volatile solvents.

Preferably the solvent is recovered and examined for purity. In a well-controlled process with adequate ventilation it can be recycled. Preferably the recovered solvent should not contain any titanium. This provides a further quality control check and also confirms binding of the coupling agent to the particulates.

When coupling an organic polymer to pigment or extender pigment, the organic polymer may comprise as little as 15 percent by weight or less of the mixture and the titanate can be present in amounts of at least 0.01 percent by weight, although from about 1 to 5 percent by weight is more practical. Preferred compositions use the microspheres in the amount of 5 to 35 percent by weight and a coupling agent, for example, isopropyl triisostearoyl titanate in amounts of 1 to 3 percent by weight. In general, however, the weight of microspheres will be from 5 to 100 percent of the weight of pigment material.

A particularly preferred embodiment of the invention employs hydrophilic-surfaced inorganic pigment materials coupled to organic polymeric microspheres.

Specific advantages of preferred pigment-material-microsphere complexes of this invention include: improved hydrophobicity; a higher melting point; more uniform specific gravity and bulk density; improved dispersibility; lower viscosities at comparable use levels; higher solids loading is possible; improved adhesion; smoother texture; unique surface area characteristics and reduced processing times and clean up is necessary.

Such coupled microspherical powders and fillers are useful in cosmetic compositions, especially oil-based and aqueous-based emulsions and poured powders. The advantages include: uniform specific gravity; a controlled oil absorption rate; lower specific surface area is achieved; maximum solid content for a given viscosity is achieved; minimum viscosity for a desired solids load is achieved; improved flowability and ease of dispersion; improved spreadability and application; a unique

surface texture (smooth/creamy) is achieved; and spherical particulate characteristics are maintained during processing. Organic polymeric microsphere materials can thus be used to better incorporate pigments and fillers, or extender pigments, into a cosmetic.

These materials also yield advantages when incorporated into pressed powders. The powders are easier to press; the oil absorption rate is better controlled; packing is reduced; adhesion is improved; density is uniform; and a smooth surface is achieved.

The polymer microspheres used in cosmetics such as polyethylene may begin to soften at 95° C. to 110° C. and then deform or melt and flow. It is not unusual for these temperatures to be realized and exceeded in the processing of cosmetics.

By treating polymer microspheres mixed with an inorganic material such as boron nitride with a titanate or other type of coupling agent, insulated microspheres are achieved. The coating acts as insulation preventing the melting or deforming of the microspheres during processing. Thus, the dispersion advantages etc., due to microspherical shape are available in the final cosmetic product.

In accordance with the inventive method of making an improved cosmetic component, one selects an organic microspherical material for cosmetic use. A pulverized inorganic material to be coupled to and carried by the organic microspherical material is combined with the microspherical material and the inorganic material to form a mixture. The liquid titanate coupling agent is added to the mixture and the resulting mixture is thoroughly mixed to form a mixture of microspherical compounds of inorganic material coupled to organic microspheres by the titanate coupling agent. Tests on specific coupled combinations have been performed and scanning electron microscope images have been made for components, mixtures and coupled mixtures.

Polyvinylidene copolymer (PVDC) microspheres have been combined with talc, with black iron oxide and with spherical silica. Isopropyl triisostearoyl titanate was used as a coupling agent. Polyethylene was coupled with boron nitride using isopropyl triisostearoyl titanate. The amount of isopropyl triisostearoyl titanate was 2 percent by weight in all cases.

Talc was mixed with PVDC in a 85 to 15 ratio. The specific surface area of the mixture was 5.2 meters²/gram, talc alone has a specific surface area of 8.0 meters²/gram. When the mixture was treated, the specific surface area was reduced to 0.57 meters²/gram.

A 20 percent composition of the treated talc-PVDC mixture in mineral oil was pourable with a measurable viscosity while a like composition using an untreated mixture formed a paste and had no flow property.

It was found that one gram of the treated material would float on 50 ml of water for more than an hour. This was not the situation without treatment. The treated mixture thus exhibits greatly increased hydrophobicity.

When PVDC and silica were combined in a 15 to 85 ratio and treated with isopropyl triisostearoyl titanate, a float time for one gram of material on the surface of water was also in excess of one hour. When an untreated mixture was floated on water, the silica swiftly separated out and sank.

Polyethylene microspheres having a melt range of 105° to 106° C. were combined in a 50 to 50 ratio with boron nitride powder and treated with isopropyl triisostearoyl titanate. Again, the titanate amount was two

percent by weight of the mixture. The melt range for the treated microspherical mixture was increased to more than 140° C.

Some preferred embodiments of the invention will now be described, by way of illustration, and without limitation, as the scope of the invention is limited only by the appended claims, with reference to the following examples, in which parts are by weight.

EXAMPLE 1

30 parts of nylon II, as described in Table 1, and 70 parts of mica were intimately blended in a vacuum blender for 5 minutes with mica ground to an average particle size of 5 microns and a specific surface area of 1.4-1.6 meters squared/gram. Sufficient 34 percent solution of isopropyl triisostearoyl titanate in Isopar C (Exxon Corporation) was sprayed onto the surface of the blended powders to coat the powder with about 2 percent by weight of isopropyl titanium triisostearate. The blender temperature was set at 80° C. and the powdered complex reaction product was dried for 1 hour. After a five minute post-process blend, and cooling, the powder was discharged from the blender.

The nylon-mica complex reaction product of treated powder has a slightly waxy odor, good slip, good adhesion to the skin, is hydrophobic and exhibits significantly reduced oil absorption (40 grams oil/100 grams) than the base uncomplexed nylon II particles. In addition, the composite powder or complex can easily be dispersed in water, like the mica, and unlike the nylon, so that the complex or composite powder acquires useful characteristics from both its parent powders.

The recovered solvent is analyzed and has a boiling point elevated by 2° C. compared with Isopar C. This difference is acceptable. The percentage of titanate bound in the composite powder product was determined to be 2 percent. No solvent odor could be detected in the product.

Evidence of the coupling treatment and its effects was also determined by resistivity measurements by applying a voltage between metal electrodes in a dry container of powder, the powder being lightly tapped to make contact at the electrodes. Various nylon microsphere materials exhibited high individual resistivities of insulative value in excess of 10^{14} ohm-cm. Mica alone showed a semiconductive resistivity value of about 1.5×10^8 ohm-cm. A 30/70 nylon/mica had a higher resistivity of about 6.6×10^{10} ohm-cm. while that of the reaction product complex of Example 1 was about 1.1×10^{13} , only about one order of magnitude less than the naked nylon microspheres. Interpreting a higher resistance to imply greater hydrophobicity, the complexing process has increased the hydrophobicity of the complex, as compared with the mix, by more than two orders of magnitude, clearly demonstrating coupling.

EXAMPLE 2

15 parts of polyvinylidene copolymer (PVDC) as described in Table 1 were added to a vacuum blender followed by 85 parts of talc pigment. The powders were intimately blended for 5 minutes. A 17 percent solution of isopropyl triisostearoyl titanate in Isopar C (Exxon Corp.) was sprayed onto the surface of the powder mix. The blender temperature was set to 80° C. and the powders were dried for 1 hour. After cooling, the treated powder was discharged to a drum and examined. The composite powder product was hydrophobic, had a slightly waxy odor, had good slip, improved adhesion,

and lower oil absorption (180 grams oil/100 grams than untreated PVDC. The PVDC powder used was hollow and very lightweight, being easily airborne. The treated material complex product or composite powder is substantially denser having an apparent density of approximately 1 gram per cubic inch, and could readily be dispensed without becoming airborne. The composite pigment material contained 2 percent isopropyl triisostearoyl titanate by weight had a generally spherical shape, there was no odor of solvent detected and the specific surface area was in the range of from 0.5 to 2 m²/g.

EXAMPLE 3

15 parts PVDC as described in Table 1 and 85 parts mica pigment material were intimately blended in a vacuum blender. The mica had been ground to an average particle size of 5 microns and had a surface area between 1.4-1.6 meters squared per gram. The powder was blended, treated, and dried as described in Example 2. The treated pigment was spherical. The treated pigment had good slip, improved adhesion, was hydrophobic, and had lower oil absorption (180 grams oil/100 grams). The solvent odor could not be detected. The amount of titanate employed was 2 percent by weight of the composition.

EXAMPLE 4

15 parts polyvinylidene copolymer (PVDC) microspheres and 85 parts of silica as described in Table 1 were intimately blended, treated and dried as described in Example 2. The microspheres are extremely lightweight and easily airborne. In contrast, the coupled powder can be easily dispensed. The apparent density of the complexed pigment material is approximately 1.4 grams/cbi. The oil absorption of the PVDC microspheres decreased to approximately 280 grams oil/100 grams. The complexed pigment material is hydrophobic, has good slip, improved adhesion, and a slightly waxy odor. There was no odor of solvent present. The amount of titanate used was 2 percent by weight. The spherical shapes were maintained.

The pigment-material-microsphere complex products of Examples 2, 3 and 4 all had a spherical appearance under a scanning electron microscope, an average particle size of about 20 micron with 90 percent of particles falling within the range of from 5 to 35 micron, and a waxy odor. Talc-, mica- and silica-PVDC complexes produced by methods generally equivalent to those of Examples 2-4 can be advantageously incorporated in anhydrous blushers, shadows, lip powders, eye pencils and lip pencils, and pressed powders. In liquid foundations such complexes are also effective, silica-PVDC complexes being especially so. The latter can also be used, with advantage in solvent or aqueous-based mascara.

In such formulations, customary proportions of pigment are used, although because of the benefits of the invention, smaller amounts may be adequate. Richer, creamier or smoother products can result with better pigment-related appearance qualities.

EXAMPLE 5

15 parts PVDC as described in Table 1 and 85 parts black iron oxide pigment were intimately mixed. The black iron oxide had been ground to an average particle size between 2-5 microns. The mixed powders were blended, treated, and dried as described in Example 2.

The spherical shape was maintained. The treated pigment has good slip, improved adhesion and texture. The amount of titanate was 2 percent by weight. There was no odor of solvent. The treated pigment was hydrophobic.

EXAMPLE 6

5 parts PVDC and 95 parts talc were intimately blended, treated, and dried as described in Example 2. The treated powder was spherical, hydrophobic, had good slip and improved adhesion. The amount of titanate was 2 percent by weight of the composition. There was no odor noticed. The complexed pigment could be more readily pressed than polyvinylidene copolymer.

EXAMPLE 7

50 parts polyethylene as defined in Table 1 were intimately mixed with 50 parts of boron nitride. 99 percent of the boron nitride particles had a particle size below 10 microns. The pigments were blended, treated, and dried as described in Example 2. The complexed pigment had good slip, improved adhesion, and was hydrophobic. The melting point of the complex was increased to about 140 centigrade. Boron nitride is believed to provide insulation to the polyethylene. The pigment complex is particularly useful for incorporation as part of a pressed powder blend. This blend can be pulverized without the polyethylene component melting. The amount of titanate was 2 percent. There was no odor of solvent in the product.

BRIEF DESCRIPTION OF THE DRAWINGS

The following scanning electron microscope photographs depict various microspheres, microsphere-irregular particulate mixtures and microspheres coupled with irregular particulates by isopropyl triisostearoyl titanate.

Photographs 1 to 8 show the shape of the particulate materials to be coupled and photographs 9, 10 and 11 depict the non-homogeneity and uneven distribution of materials in a non-coupled mixture. Such inhomogeneity leads to uneven dispersion, accelerated separation and other problems. Photographs 12 to 27 show the coupled mixtures and the spherical nature of the microspheres remaining intact after being coated with the irregularly shaped material. The materials depicted and the magnification employed in the photomicrographs are detailed in the legends accompanying each of photographs 1-27. Scales in microns are also shown for approximate determination of actual particle size characteristics directly from the photographs. Scanning electron micrographs or photographs 28 and 29 show 70% mica coupled to microspherical ethylene/acrylates copolymer using an organofunctional silane coupling agent at magnifications of 500 and 6,000 respectively.

The inorganic materials are much denser than the organic polymers and therefore significant loading in terms of weight of the inorganic material is achievable while maintaining the spherical shape of the coupled materials.

The invention has been described with special reference to the field of cosmetics where it provides outstanding benefits, as set forth herein. It will be clear, however, to workers in other fields that some of the unique benefits of the pigment-material-microsphere complexes of this invention are transferable to and realizable in other fields. For example, in compounding moldable plastics or rubbers, good dispersibility of pig-

ment materials is desirable and the unique three-dimensional control of spatial distribution that is afforded by the microsphere-complexed pigment materials of this invention is also valuable in those fields. Such control affords the prospect of better utilization of pigment materials exploiting the advantages described herein. Accordingly, the invention extends to plastics and rubber materials, cured and uncured, molded and amorphous, as well as paints, inks and artists' materials which incorporate novel pigment-material-microsphere complexes such as those described hereinabove in a manner equivalent to the cosmetic materials described herein.

While an illustrative embodiment of the invention has been described above, it is, of course, understood that various modifications will be apparent to those of ordinary skill in the art. Such modifications are within the spirit and scope of the invention, which is limited and defined only by the appended claims.

I claim:

1. An improved cosmetic compound consisting essentially of a pigment material and microsphere complex of bulk density less than said pigment material's bulk density, said microsphere complex comprising:

- a) microsphere-material particles having an average particle size less than 1000 microns;
- b) a plurality of organic or inorganic pigment particles covalently bonded to each said microsphere particle; and
- c) a coupling agent residue extending between said pigment particles and each said microsphere particle whereby said pigment particles are covalently bonded to said microsphere particles;

one of said microsphere or said pigment materials being an organic material and the other being inorganic, and said coupling agent residue being derived from a coupling agent reactive with said microsphere particles and reactive with said pigment material particles.

2. A cosmetic compound according to claim 1, said compound having a surface area-to-volume ratio lower than a corresponding mixture of said pigment and microsphere materials, wherein said microsphere material particles comprise from 5 to 35 weight percent of an organic polymeric microspherical powder, said pigment material comprises a pulverized inorganic cosmetic pigment material of particles smaller than said organic polymeric microsphere material and wherein said coupling agent from which said coupling agent residue is derived comprises from 1 to 5 weight percent of a titanate coupling agent, said coupled product having a generally spherical particulate shape, said inorganic cosmetic material and said cosmetic material being capable of being coupled by said titanate coupling agent and said weight percentages being based on the weight of said cosmetic compound.

3. An improved cosmetic material according to claim 2 wherein said organic polymeric material is selected from the group consisting of microspherical polyethylene, polymethyl methacrylate, nylon, ethylene acrylates copolymer, polyurethane and polyvinylidene copolymers.

4. An improved cosmetic compound as claimed in claim 2, wherein said inorganic cosmetic pigment material is a cosmetically acceptable insulating material.

5. An improved cosmetic compound as claimed in claim 4, wherein said cosmetically acceptable insulating material is boron nitride.

6. An improved cosmetic compound as claimed in claim 2, wherein said titanate coupling agent is a liquid monoalkoxy (C₁ to C₂₀) isostearoyl titanate.

7. An improved cosmetic compound as claimed in claim 6, wherein said liquid titanate coupling agent is isopropyl triisostearoyl titanate.

8. An improved cosmetic compound as claimed in claim 2, wherein said pigment material is selected from the group consisting of inorganic pigments, pigment extenders, talc, sericites, silica and mica.

9. A pigment-material-microsphere complex according to claim 1 wherein said pigment material particles are polar particles having active sites, said microsphere particles are non-polar and said coupling agent is adapted for coupling polar particles having active sites to non-polar particles and has the general formula:



where M is a carrier moiety with a valency state of from 2 to 6, preferably from 2 to 4; n and m is each from 1 to 5 with n+m equaling said valency state; X is a polar-reactive ligand reactable with said active sites on said polar particles and Y is a non-polar-reactive ligand reactable with said non-polar particles.

10. A pigment-material-microsphere complex according to claim 9 wherein a residue of said coupling agent coats said inorganic pigment material particles.

11. A method of making an improved pigment material of reduced specific surface area said material being a pigment-material-microsphere complex having a specific surface area less than that of a respective uncomplexed pigment material said method comprising the steps of:

- a) selecting a microsphere material to serve as a carrier for said pigment;
- b) pulverizing or obtaining a pulverized pigment material to be carried by said microsphere material;
- c) combining said microsphere material and said pigment material to form a mixture;
- d) adding a coupling agent to the mixture, said coupling agent having a first ligand reactive with said microsphere particles and a second ligand reactive with said pigment material particles;

e) thoroughly mixing said microsphere material, said pigment material and said coupling agent under conditions to couple said pigment material to said microspheres by reaction of said first and second ligands; and

f) recovering said pigment-material-microsphere complex from the product of e).

12. A method according to claim 11 wherein said microsphere material comprises organic polymeric microspheres and said pigment material is inorganic.

13. A method according to claim 11 wherein said microsphere material is inorganic and said pigment material is organic.

14. A method according to claim 11 wherein said coupling agent is an organofunctional liquid titanate.

15. A method according to claim 11 wherein said coupling agent is an organofunctional silane.

16. A method according to claim 11 comprising the steps of spraying said coupling agent in solution on said mixture of microspherical and pigment material.

17. A method according to claim 14 wherein said liquid titanate coupling agent is dissolved in an isoparaffinic solvent having a distillation range substantially between 97° and 140° C.

18. A method according to claim 14 wherein said microsphere material comprises from 5 to 100 percent of the weight of the pigment material and said coupling agent comprises from 0.01 to 5 weight percent.

19. A method according to claim 14 wherein said microsphere material comprises from 15 to 35 percent of the weight of the pigment material and said coupling agent comprises from 1.0 to 5 weight percent.

20. An improved cosmetic compound consisting essentially of a microsphere-to-microsphere material complex said complex having a specific surface area less than that of corresponding uncomplexed microsphere material and comprising individual complex particles having multiple microspheres of average particle size less than 1000 microns covalently bonded to a single microsphere by means of a coupling agent residue extending between each said multiple microsphere and each said single microsphere and said coupling agent residue being derived from a coupling agent reactive with said microsphere particles.

* * * * *



US005169442A

United States Patent [19]

Noguchi et al.

[11] **Patent Number:** **5,169,442**[45] **Date of Patent:** **Dec. 8, 1992**[54] **BLUISH GREEN PIGMENT AND METHOD
OF PREPARING THE SAME**[75] **Inventors:** Tamio Noguchi; Yumiko Waragai,
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Fed. Rep. of Germany[21] **Appl. No.:** 705,000[22] **Filed:** May 24, 1991[30] **Foreign Application Priority Data**

May 24, 1990 [JP] Japan 2-132724

[51] **Int. Cl.:** C04B 14/20[52] **U.S. Cl.:** 106/417; 106/415;
106/416; 424/63; 424/69; 424/401; 428/363;
428/379[58] **Field of Search** 424/401, 63, 69;
106/415, 416, 417; 428/363, 379[56] **References Cited****U.S. PATENT DOCUMENTS**4,603,047 7/1986 Watanabe et al. 424/63
4,772,331 9/1988 Noguchi et al. 106/417**FOREIGN PATENT DOCUMENTS**

63-265966 11/1988 Japan .

Primary Examiner—Thurman K. Page*Assistant Examiner*—Robert H. Harrison*Attorney, Agent, or Firm*—Millen, White, Zelano and
Branigan[57] **ABSTRACT**

The invention relates to a bluish green pigment comprising a flaky fine powder as a substrate, in which the substrate is coated with a metal oxide composite composed of oxides of magnesium, calcium, cobalt and titanium in a coated amount of from 5 to 70% by weight on the basis of the total pigment.

6 Claims, No Drawings

BLUISH GREEN PIGMENT AND METHOD OF PREPARING THE SAME

BACKGROUND OF THE INVENTION

The present invention relates to a bluish green pigment as coated with a metal oxide composite, which has a good color tone with excellent saturation and lightness and has high chemical safety, as well as to a method of preparing the same. The object of the present invention is to provide a bluish green pigment which is useful as a colorant for cosmetic materials, coating compositions, inks and plastics.

Green or bluish green flaky pigments, prepared by coating a blue or green pigment such as prussian blue or ultramarine pigment or chromium oxide on the surface of a flaky mica or a flaky mica as coated with a titanium oxide having an interference color of blue or green, as well as a colored flaky powder prepared by coating a metal oxide composite comprising oxides of titanium, cobalt and lithium on the surface of a flaky powder have been known.

Also known is a cobalt (II) ion-containing green pigment, specifically a spinel type titanium pigment such as cobalt titanate ($\text{Co}_2\text{TiO}_4\text{-CoTiO}_3$), which is obtained by blending a cobalt oxide powder and a titanium oxide powder and then firing the resulting blend at a high temperature of 900° C. or higher. Additionally, green pigments with improved color tone such as cobalt lithium titanate ($\text{Li}_2\text{CoTi}_3\text{O}_8$) and a composition of $\text{CaTiO}_3\text{-CoTiO}_3\text{-TiO}_2$ are also known.

A bluish green pigment, having a chemical formula of XCoO(2-X)MgOTiO_2 (X is from 0.8 to 1.0; and the main wavelength λ_p is from 491 to 500 μm) is known, and is prepared by reacting magnesium oxide and titanium oxide at a high temperature of about 1300° C. to synthesize magnesium titanate (MgTiO_3) having a spinel structure and doping cobalt oxide to the titanate by firing.

It is not possible to produce this pigment on a flaky substrate, however, such as in a process wherein a substrate of a flaky kaolin, talc, sericite or mica is coated with a cobalt (II) ion-containing spinel type titanium pigment, the flaky substrate is blended with cobalt oxide, magnesium oxide and titanium oxide and then fired at a high temperature. In this process, the flaky substrate and the oxides are solidified by firing, and a pigment is not obtained.

A green pigment prepared by coating a flaky powder with a metal oxide composite comprising oxides of titanium, cobalt and lithium is known (Japanese Patent Application Laid-Open No. 63-043963). However, lithium is an extremely scarce natural resource and is therefore high-priced as an industrial raw material. Additionally, the process of producing the pigment comprises complicated wet-process steps and dry-process steps where a titanium oxide hydrate and a cobalt oxide hydrate are precipitated on the surface of the flaky powder by a wet-process, then the thus precipitate-coated product is washed with water and dried to give a powder and the resulting powder is blended with a lithium compound and then fired at a high temperature. Consequently, the pigment is inevitably high-priced.

On the other hand, the above-mentioned pigment as prepared by coating a prussian blue on the surface of a titanium oxide-coated mica has some drawbacks that the coated prussian blue fades in an alkaline solution generating dicyan or is decomposed to fade under heat

at a temperature of 200° to 300° C. Similarly, the pigment as coated with ultramarine has a problem of chemical stability, since it generates hydrogen sulfide gas in an acidic solution. The use of the other pigment as coated with chromium oxide is limited currently since chromium is said to have a problem of safety.

SUMMARY OF THE INVENTION

The present inventors earnestly and repeatedly studied so as to overcome the above-mentioned drawbacks and problems in the prior art and, as a result, have found that a bluish green pigment having high intensity and saturation and having good safety and stability can be obtained by a simple operation and inexpensively, by coating a substrate of a flaky fine powder with a metal oxide composite comprising oxides of titanium, cobalt, magnesium and calcium. The present invention has been completed on the basis of such finding.

Specifically, the present invention provides a bluish green pigment comprising a flaky fine powder as a substrate, in which the substrate is coated with a metal oxide composite composed of oxides of magnesium, calcium, cobalt and titanium in a coated amount of from 5 to 70% by weight on the basis of the total pigment. It further provides a method of preparing the bluish green pigment, where an aqueous solution containing a magnesium salt, a calcium salt, a cobalt salt and a titanium salt dissolved therein and an aqueous basic solution are added to a suspension of a flaky fine powder as suspended in water with heating and stirring whereby hydroxides and oxide hydrates of the said metals and optionally carbonates of calcium are co-precipitated on the surface of the flaky fine powder substrate, and the resulting product is taken out by filtration, washed with water and fired.

The present invention will be explained in detail hereunder.

The present pigments all are based on a flaky powder substrate, whereas the cobalt-containing pigments discussed in the "Background" section are conventional, carrier-free pigments.

First, the method of preparing a bluish green pigment of the present invention will be explained in detail. A flaky powder of mica, talc, kaolin, sericite or synthetic mica is suspended in water; an aqueous solution containing a magnesium salt, a calcium salt, a cobalt salt and a titanium salt dissolved therein, or an aqueous solution containing metal ions of magnesium(II), calcium(II), cobalt(II) and titanium(IV), and an aqueous basic solution are added to the suspension with heating and stirring, whereupon the pH value of the suspension is adjusted to be within the range of from 1.0 to 2.5 and a titanium oxide hydrate containing a small amount of magnesium(II) ion, calcium(II) ion and cobalt(II) ion is coated on the surface of the flaky fine powder substrate; then an aqueous basic solution is gradually added to the suspension so that the pH value of the suspension is made to be within the range of from 2.5 to 7.0; and an aqueous basic solution is further added thereto so that the pH value comes to within the range of from 7.0 to 10.0, whereby cobalt oxide hydrate, calcium hydroxide and magnesium hydroxide are co-precipitated on the surface of the said titanium oxide hydrate-coated flaky substrate to thereby completely coat the surface of the flaky fine powder substrate with cobalt(II) ion, as a cobalt oxide hydrate.

As the above-mentioned aqueous basic solution, an aqueous solution containing an alkali metal carbonate or urea may be used whereby carbonates such as cobalt carbonate, calcium carbonate and magnesium carbonate may be co-precipitated on the surface of the said titanium oxide hydrate-coated flaky substrate.

In the next step, the flaky substrate as coated with co-precipitates of hydroxides and oxide hydrates of the above-mentioned metals and optionally carbonates is removed from solution by filtration, washed with water and fired, whereby an intended bluish green pigment as coated with a metal oxide composite comprising oxides of magnesium, calcium, cobalt and titanium is obtained efficiently.

As examples of the flaky fine powder which is used as a raw material in preparing the pigment of the present invention, there are mentioned clay minerals such as kaolin, talc, sericite, mica and pyrophyllite, as well as synthetic mica. Additionally, a titanium oxide-coated mica pigment or an iron oxide-coated mica pigment which are generally sold as commercial products may directly be used as the raw material in the present invention. In this case, titanium ions need not be present in the salt solution; the other metals diffuse into the existing titanium layer to form the composite upon firing.

As examples of the above-mentioned magnesium salt, there are mentioned magnesium chloride, magnesium bromide, magnesium sulfate and magnesium nitrate; as those of the calcium salt, there are calcium chloride and calcium nitrate; as those of the cobalt salt, there are cobalt chloride, cobalt sulfate and cobalt nitrate, and as those of the titanium salt, there are titanium tetrachloride and titanium sulfate. These inorganic salts of metals are preferably used in the present invention.

As other examples of the magnesium salt, calcium salt, cobalt salt and titanium salt, there are further mentioned alkoxides such as titanium tetrapropoxide $Ti(C_3H_7O)_4$, as well as salts of metals with organic acids. Examples of the above-mentioned basic compound, which is employed for pH-adjustment in the step of coating the metal ions on the surface of the flaky substrate as their hydroxides or oxide hydrates, are hydroxides such as sodium hydroxide, potassium hydroxide and ammonium hydroxide, carbonates such as sodium carbonate, potassium carbonate and ammonium carbonate, as well as hydrogencarbonates thereof. Additionally, urea which is hydrolyzed by heating in an aqueous solution to give ammonia and carbon dioxide may also be referred to. In particular, where urea is used, carbon dioxide to be generated by hydrolysis is bonded to calcium(II) ion to give calcium carbonate and the carbonate is co-precipitated on the surface of the substrate along with other cobalt oxide hydrate, magnesium hydroxide and titanium oxide hydrate. In this case, a pigment having a better dispersibility can be obtained.

Where a commercial product of titanium dioxide-coated mica pigment or iron oxide-coated pearly mica pigment (for example, Iridin, Timiron or Colorona by Merck Co.) is used as the flaky fine powder substrate, a two-coloring pearly pigment which is new and which has a color hue variable in accordance with the reflected light or transmitted light as imparted thereto can be obtained. For instance, a titanium dioxide-coated mica pigment having a red color to reflected light and a green color to transmitted light is coated with the above-mentioned metal oxide composite, the resulting pigment has a bluish red color to reflected light and a yellowish green color to transmitted light.

The bluish green pigment of the present invention may have various color tones which vary in a broad range of from a bluish green color to a green color in accordance with selection and combination of the conditions of the grain form and/or size of oxides of titanium, cobalt, magnesium and calcium to be coated on the surface of the flaky fine powder substrate, the amount of the metal oxide composite coated, as well as the heating temperature and the heating time in preparing the pigment. Production of a desired color may be achieved by routine experimentation, e.g., in accordance with the examples.

The amount of the above-mentioned metal oxide composite to be coated on the surface of the flaky substrate is preferably from 5 to 70% by weight, more preferably from 10 to 60% by weight, to the whole pigment. If the coated amount is less than 5% by weight, a pigment having a good saturation is generally not obtained. On the other hand, if the coating is more than 70% by weight, coagulated solids tend to form during preparation and a pigment with a good quality is generally not obtained.

After the surface of the above-mentioned flaky substrate has been coated with hydroxides and oxide hydrates of titanium, cobalt, magnesium and calcium optionally along with carbonates of the metals, the thus coated substrate is fired to finally form oxides of the metals on the substrate, whereupon the firing temperature is from 500° to 1300° C., preferably 700° to 1000° C., and the firing time is 0.5 to 5.0 hours.

Under the above-mentioned condition, oxides of titanium, cobalt, magnesium and calcium form a composite oxide of the so-called "solid solution" form. In addition, oxides of the respective metals per se may also be present along with the composite oxide. In the present invention, the term "metal oxide composite" includes all of these cases.

The composition of the metal oxide composite in the bluish green pigment of the present invention generally comprises from 0.3 to 1.0 mole of cobalt oxide, from 0.05 to 0.20 mole of magnesium oxide and from 0.05 to 0.20 mole of calcium oxide based on one mole of titanium oxide. Accordingly, the proportion of the raw materials to be reacted is preferably selected in the same proportions so as to produce this composition.

The bluish green pigment of the present invention is obtained by the method mentioned in detail in the above. As the pigment has an excellent color tone with good intensity and saturation and is non-toxic and additionally has various excellent characteristics of light fastness, heat resistance and chemical resistance, it is an industrially useful and advantageous colorant for cosmetic materials, coating compositions, plastic products, ink products and ceramic products.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

In the foregoing and in the following examples, all temperatures are set forth uncorrected in degrees Celsius and unless otherwise indicated, all parts and percentages are by weight.

The entire disclosures of all applications, patents and publications, cited above and below, and of corresponding application Japanese Patent Appln. No. 0/132724,

filed May 24, 1990, are hereby incorporated by reference.

EXAMPLES

Example 1

A suspension prepared by adding 120 g of a fine muscovite powder having a grain size of from 10 to 60 microns to 1200 ml of water was heated at 95° C., and 295.5 g of aqueous 32 wt. % titanium tetrachloride solution and an aqueous solution prepared by dissolving 31.6 g of cobalt chloride hexahydrate, 5 g of magnesium chloride hexahydrate and 3.7 g of calcium chloride dihydrate were added to the suspension with adjusting the pH value of the suspension to fall within the range of from 1.0 to 2.5 with an aqueous 10 wt. % sodium hydroxide solution, with heating and stirring, over a period of 7 hours. After all the above-mentioned aqueous metal salt solutions were added, the pH value of the suspension was adjusted to fall within the range of from 7 to 10 by adding an aqueous 10 wt. % sodium hydroxide solution thereto, whereby hydroxides and oxide hydrates of the metals were co-precipitated on the surface of the fine muscovite powder. The resulting product was then taken out by filtration, washed with water and dried at 105° to 110° C. for 8 hours. Next, the product was fired at 800° C. for one hour to obtain a bluish green pigment in which the surface of the fine muscovite powder was coated with the metal oxide composite.

Example 2

A suspension prepared by adding 120 g of a fine sericite powder having a grain size of from 1 to 20 microns to 1200 ml of water was heated to 95° C., and 295.5 g of aqueous 32 wt. % titanium tetrachloride solution and an aqueous solution prepared by dissolving 31.6 g of cobalt chloride hexahydrate, 5 g of magnesium chloride hexahydrate and 3.7 g of calcium chloride dihydrate in 3000 ml of water were added to the suspension with adjusting the pH value of the suspension to fall within the range of from 1.0 to 2.5 with an aqueous 10 wt. % sodium hydroxide solution, with heating and stirring, over a period of 7 hours. After all the above-mentioned aqueous metal salt solutions were added, the pH value of the suspension was adjusted to fall within the range of from 7 to 10 by further adding an aqueous 10 wt. % sodium hydroxide solution thereto, whereby hydroxides and oxide hydrates of the metals were co-precipitated on the surface of the fine sericite powder. The resulting product was then taken out by filtration, washed with water and dried at 105° to 110° C. for 8 hours. Next, the product was fired at 800° C. for one hour to obtain a bluish green pigment in which the surface of the fine sericite powder was coated with the metal oxide composite.

Example 3

A suspension prepared by adding 70 g of a fine synthetic mica powder having a grain size of from 1 to 70 microns to 700 ml of water was heated at 95° C., and 110 g of an aqueous 32 wt. % titanium tetrachloride solution and an aqueous solution prepared by dissolving 10 g of cobalt chloride hexahydrate, 2 g of magnesium chloride hexahydrate and 2 g of calcium chloride hexahydrate in 150 ml of water were added to the resulting suspension with adjusting the pH value of the suspension to fall within the range of from 1.0 to 2.5 with an aqueous 10 wt. % sodium hydroxide solution, with heating and stirring, over a period of 2 hours. After all

the above-mentioned aqueous metal salt solutions were added, the pH value of the suspension was adjusted to fall within the range of from 7 to 10 by further adding an aqueous 10 wt. % sodium hydroxide solution thereto, whereby hydroxides and oxide hydrates of the metals were co-precipitated on the surface of the fine talc powder. The resulting product was taken out by filtration, washed with water and dried at 105° to 110° C. for 8 hours. Next, the product was fired at 800° C. for one hour to obtain bluish green pigment in which the surface of the fine talc powder was coated with the metal oxide composite.

Example 5

A suspension prepared by adding 120 g of a fine kaolin powder (K. clay, product by Shokosan Mining Industry) having a grain size of 12 microns or less to 1200 ml of water was heated at 95° C., and 98.5 g of an aqueous 32 wt. % titanium tetrachloride solution and an aqueous solution prepared by dissolving 31.6 g of cobalt chloride hexahydrate, 3.5 g of magnesium chloride hexahydrate and 2.5 g of calcium chloride dihydrate in 1000 ml of water were added to the suspension with adjusting the pH value of the suspension to fall within the range of from 1.0 to 2.5 with an aqueous 10 wt. % sodium hydroxide solution, with heating and stirring, over a period of 2 hours. After all the above-mentioned and aqueous metal salt solutions were added, the pH value of the suspension was adjusted to fall within the range of from 7 to 10 by further adding an aqueous 10 wt. % sodium hydroxide solution, whereby hydroxides and oxide hydrates of the metals were co-precipitated on the surface of the fine kaolin powder. The resulting product was taken out by filtration, washed with water and dried at 105° to 110° C. for 8 hours. Next, the product was fired at 850° C. for one hour to obtain a bluish green pigment in which the surface of the fine kaolin powder was coated with the metal oxide composite.

Example 6

A suspension prepared by adding 120 g of a titanium oxide-coated fine mica powder having a blue-reflecting color and an yellow-transmitting color (Iriodin 225, product by Merck Co.) to 1200 ml of water was heated at 95° C., and 98.5 g of an aqueous 32 wt. % titanium tetrachloride solution and an aqueous solution prepared by dissolving 31.6 g of cobalt chloride hexahydrate, 3.5 g of magnesium chloride hexahydrate and 2.5 g of calcium chloride dihydrate in 100 ml of water were added to the suspension with adjusting the pH value of the suspension to fall within the range of from 1.0 to 2.5 with an aqueous 10 wt. % sodium hydroxide solution, with heating and stirring, over a period of 2 hours. After all the above-mentioned aqueous metal salt solutions were added, the pH value of the suspension was adjusted to fall within the range of from 7 to 10 by further adding an aqueous 10 wt. % sodium hydroxide solution thereto, whereby hydroxides and oxide hydrates of the metals were co-precipitated on the surface of the titanium oxide-coated fine mica powder. The resulting product was taken out by filtration, washed with water and dried at 105° to 110° C. for 8 hours. Next, the product was fired at 850° C. for one hour to obtain a brilliant bluish green pigment in which the surface of the titanium oxide-coated fine mica powder was coated with the metal oxide composite. The pigment thus obtained

had a bluish green-reflecting color with a high saturation and had an yellowish red-transmitting color.

Example 7

A suspension prepared by adding 120 g of a titanium oxide-coated fine mica powder having a gold-reflecting color and a blue-transmitting color (Iridin 205, product by Merck Co.) to 1200 ml of water was heated at 95° C., and 98.5 g of an aqueous 32 wt. % titanium tetrachloride solution and an aqueous solution prepared by dissolving 31.6 g of cobalt chloride hexahydrate, 3.5 g of magnesium chloride hexahydrate and 2.5 g of calcium chloride dehydrate in 100 ml of water were added to the suspension with adjusting the pH value of the suspension to fall within the range of from 1.0 to 2.5 with an aqueous 10 wt. % sodium hydroxide solution, with heating and stirring, over a period of 2 hours. After all the above-mentioned aqueous metal salt solutions were added, the pH value of the suspension was adjusted to fall within the range of from 7 to 10 by further adding an aqueous 10 wt. % sodium hydroxide solution thereto, whereby hydroxides and oxide hydrates of the metals were co-precipitate on the surface of the titanium oxide-coated fine mica powder. The resulting product was taken out by filtration, washed with water and dried at 105° to 110° C. for 8 hours. Next, the product was fired at 850° C. for one hour to obtain a brilliant bluish green pigment in which the surface of the iron oxide-coated fine mica powder was coated with the metal oxide composite. The pigment thus obtained had a reddish violet-reflecting color with a high saturation and had an yellowish green-transmitting color.

Example 8

A suspension prepared by adding 60 g of an iron oxide-coated fine mica powder (Iridin 500, product by Merck Co.) to 600 ml of water was heated at 95° C., and 100 g of an aqueous 32 wt. % titanium tetrachloride solution and an aqueous solution prepared by dissolving 12 g of cobalt chloride hexahydrate, 1.6 g, of magnesium chloride hexahydrate and 1.2 g of calcium chloride dihydrate in 100 ml of water were added to the suspension with adjusting the pH value of the suspension to fall within the range of from 1.0 to 2.5 with an aqueous 10 wt. % sodium hydroxide solution, with heating and stirring, over a period of 2 hours. After all the above-mentioned aqueous metal salt solutions were added, the pH value of the suspension was adjusted to fall within the range of from 7 to 10 by further adding an aqueous 10 wt. % sodium hydroxide solution thereto, whereby hydroxides and oxide hydrates of the metals co-precipitated on the surface of the iron oxide-coated fine mica powder. The resulting product was taken out by filtration, washed with water and dried at 105° to 110° C. for 8 hours. Next, the product was fired at 850° C. for one hour to obtain a bluish green pigment in which the surface of the iron oxide-coated fine mica powder was coated with the metal oxide composite. The color of the pigment thus obtained was more bluish green than the color hue of the iron oxide-coated fine mica powder used as the starting material.

Example 9

A suspension prepared by adding 120 g of a titanium oxide-coated fine mica powder having a blue-reflecting color and an yellow-transmitting color (Iridin 225, product by Merck Co.) to 1200 ml of water was heated

at 95° C., and 98.5 g of an aqueous 32 wt. % titanium tetrachloride solution and an aqueous solution prepared by dissolving 31.6 g of cobalt chloride hexahydrate, 3.5 g of magnesium chloride hexahydrate and 2.5 g of calcium chloride dehydrate in 100 ml of water were added to the suspension with adjusting the pH value of the suspension to fall within the range of from 1.0 to 2.5 with an aqueous 30 wt. % potassium carbonate solution, with heating and stirring, over a period of 2 hours. After all the above-mentioned aqueous metal salt solutions were added, the pH value of the suspension was adjusted to fall within the range of from 7 to 10 by further adding coated fine mica powder. The resulting product was taken out by filtration, washed with water and dried at 105° to 110° C. for 8 hours. Next, the product was fired at 850° C. for one hour to obtain a brilliant bluish green pigment in which the surface of the titanium oxide-coated fine mica powder was coated with the metal oxide composite. The pigment thus obtained had a bluish green-reflecting color with a high saturation and had a yellowish red-transmitting color.

Example 10

A suspension prepared by adding 80 g of a titanium oxide-coated fine mica powder having a blue-reflecting color and a yellow-transmitting color (Iridin 225, product by Merck Co.) to 800 ml of water was heated at 95° C., and 45 g of urea, 65.8 g of an aqueous 32 wt. % titanium chloride solution and a solution prepared by dissolving 8 g of cobalt chloride hexahydrate, 8 g of magnesium chloride hexahydrate and 12 g of calcium chloride dihydrate in 400 ml of water were added to the suspension with adjusting the pH value of the suspension to fall within the range of from 1.0 to 2.5 with an aqueous 10 wt. % sodium hydroxide solution, with heating and stirring, over a period of 40 minutes. After all the above-mentioned aqueous salt solutions were added, the pH value of the suspension was adjusted to fall within the range of from 7 to 10 by further adding an aqueous 10 wt. % sodium hydroxide solution thereto, whereby hydroxides, oxide hydrates and carbonates of the metals were co-precipitated on the surface of the titanium oxide-coated fine mica powder. The resulting product was taken out by filtration, washed with water and dried at 105° to 110° C. for 8 hours. Next, the product was fired at 800° C. for one hour to obtain a brilliant bluish green pigment in which the surface of the titanium oxide-coated fine mica powder was coated with the metal oxide composite. The pigment thus obtained had a bluish green-reflecting color with a high saturation and had a yellowish red-transmitting color.

The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

What is claimed is:

1. A bluish green pigment comprising a substrate of a flaky fine powder coated with a metal oxide composite comprising 0.3 to 1.0 mole cobalt oxide, 0.05 to 0.2 mole magnesium oxide and 0.05 to 0.20 mole calcium oxide, per mole of titanium oxide, said metal oxide composite

being produced by simultaneous precipitation of the metals onto the substrate.

2. A pigment according to claim 1, wherein the composite is present in an amount of about 5 to 70% by weight on the basis of the total pigment.

3. A pigment according to claim 1, wherein the substrate is mica, talc, kalin, sericite or synthetic mica.

4. A pigment according to claim 1, wherein substrate is a flaky fine powdered mica coated with titanium oxide.

5. A pigment according to claim 1, wherein the substrate is a flaky fine powdered mica coated with an iron oxide hydrate or iron oxide.

6. In a cosmetic composition comprising a cosmetically acceptable carrier and a pigment, the improvement wherein the pigment is one of claim 1.

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United States Patent [19]

Hashimoto et al.

[11] Patent Number: 5,030,445

[45] Date of Patent: Jul. 9, 1991

[54] COSMETIC COMPOSITION

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[21] Appl. No.: 282,967

[22] Filed: Dec. 6, 1988

Related U.S. Application Data

[63] Continuation of Ser. No. 89,075, Aug. 25, 1987, abandoned.

[51] Int. Cl.⁵ A61K 7/021; A61K 7/027; A61K 7/42; A61K 7/48

[52] U.S. Cl. 424/59; 424/60; 424/63; 424/64; 424/69; 514/847; 514/873

[58] Field of Search 424/59, 63, 69, 64

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[57] ABSTRACT

A cosmetic composition which comprises kaolin particles coated with titanium dioxide and one or more other conventional cosmetic ingredients.

3 Claims, No Drawings

COSMETIC COMPOSITION

This application is a continuation of U.S. application Ser. No. 089,075, filed Aug. 25, 1987, now abandoned.

FIELD OF THE INVENTION

The present invention relates to a cosmetic composition useful for preventing sunburn and suntan.

BACKGROUND OF THE INVENTION

Titanium dioxide powder has been widely used heretofore in various cosmetic compositions. Since finely granulated titanium dioxide particles having a maximum particle size of not more than 0.1μ , and an average particle size of 5 to 50μ show remarkable ultraviolet rays screening effect, recently, the use thereof in an anti-sunburn and anti-suntan cosmetic has been studied.

However, such finely granulated titanium dioxide particles have a large surface energy. Therefore, when a cosmetic is produced by using such titanium dioxide particles, it is difficult to uniformly disperse the particles in the cosmetic and the particles tend to form agglomerates during storage. Further, there are serious problems in the use of the finely granulated titanium dioxide particles as an ingredient for a cosmetic. For example, when it is formulated into a cake type foundation which is applied with water, the cosmetic is not uniformly applied to the skin upon use, which results in very bad finish.

OBJECTS OF THE INVENTION

Under these circumstances, the present inventors have studied intensively to obtain a cosmetic composition in which titanium dioxide having excellent ultraviolet rays screening effect are uniformly and stably dispersed. As the result, it has been found that the above problems in finely granulated titanium dioxide particles can be solved by using the titanium dioxide as a coating of kaolin particles.

SUMMARY OF THE INVENTION

According to the present invention, there is provided a cosmetic composition comprising titanium dioxide and other conventional cosmetic ingredients. The cosmetic composition of the present invention is characterized by using kaolin particles coated with titanium dioxide as said titanium dioxide.

In the cosmetic composition of the present invention, a larger amount of titanium dioxide can be formulated in comparison with a composition wherein titanium dioxide particles and kaolin particles are separately formulated. Therefore, the cosmetic composition of the present invention shows much higher ultraviolet rays screening effect and further it is homogeneous and stable. Furthermore, when the composition is applied to the skin, it gives very good finish and very good appearance as well as excellent anti-sunburn and anti-suntan effect.

DETAILED DESCRIPTION OF THE INVENTION

The kaolin particles coated with titanium dioxide used in the composition of the present invention can be prepared by adding a prescribed amount of kaolin particles having an average particle size of 0.5 to 30μ to an appropriate titanium salt such as titanium sulfate, titanium tetrachloride or the like, hydrolyzing the titanium

salt in the presence of kaolin, and then, after filtration, washing and drying of the hydrolized mixture according to a conventional manner, calcining the mixture at about 300°C . to 90°C . for 10 to 180 minutes. For example, kaolin (135 g) having an average particle size of 2μ is added to an aqueous solution of titanyl sulfate (1 liter) containing 15 g/liter of titanyl sulfate calculated as TiO_2 and the mixture is boiled with stirring for 2 hours. The product is filtered and washed with water. The resulting cake is separated and dried at 110°C . It is further calcined at about 800°C . for 30 minutes to obtain a desired kaolin particles coated with titanium dioxide.

In the kaolin particles coated with titanium dioxide thus obtained, surface of the matrix, the kaolin particle, is covered with fine particles of titanium dioxide.

Now, a cream containing the kaolin particles coated with titanium dioxide was prepared and its ultraviolet rays screening effect (SPF: Sun Protection Factor), transparency, blooming, and stability were compared with those of a cream prepared by the same manner except that a mixture of conventional finely granulated titanium dioxide particles having an average particle size of 8μ and kaolin was used instead of the kaolin particles. The results are shown in the following Table 1.

Further, according to the same manner as described above, SPF, dispersibility during preparation, and difference in a tint and finish upon use of a cake type foundation prepared by using the kaolin particles coated with titanium dioxide were evaluated. The results are shown in the following Table 2.

In the following description, all "%s" are by weight unless otherwise stated.

Each cosmetic composition was obtained according to the following formulation and preparation.

(a) Formulation of cream

Ingredient A	Amount (%)
Solid paraffin	5.0
Beeswax	4.0
Microcrystalline wax	4.0
Vaseline	7.0
Squalane	30.0
Polyoxyethylene sorbitan monolaurate (20 EO)	1.0
Sorbitan sesquileate	4.0
Ingredient B	
Distilled water	remainder
Ingredient C	
Kaolin coated with titanium dioxide [I] or a mixture of titanium dioxide and kaolin [II] (ratio of titanium dioxide in [I] or [II] is shown in Table 1)	see Table 1
Talc	5.0

The ingredients of C were homogeneously mixed and the ingredient of B is added to the mixture and thoroughly dispersed therein at 70°C . Separately, the ingredients of A were mixed and molten by heating at 70°C . and the above mixture was added thereto. The resulting mixture was emulsified with a homomixer. After emulsification, the mixture was cooled to 30°C . to obtain a cream.

(b) Formulation of cake type foundation

Ingredient A	Amount (%)
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-continued

(b) Formulation of cake type foundation	
	Amount (%)
Kaolin coated with titanium dioxide [I] or a mixture of titanium dioxide and kaolin [II] (ratio of titanium dioxide in [I] or [II] is shown in Table 1)	see Table 1
Talc	remainder
Red oxide of iron	1.0
Yellow oxide of iron	2.5
Black oxide of iron	0.05
Ingredient B	
Liquid paraffin	8.5
IPP	1.0
Sorbitan sesquioleate	3.0
Propylene glycol	2.5
Paraben	0.2
Ingredient C	
Perfume	0.25

The above ingredients of A were stirred with Henschel mixer for 5 minutes. The ingredients of B which has been molten with heating at 70° C. in a separate vessel were added dropwise to the mixture of the ingredients of A with stirring. The ingredient of C was added to the resulting mixture and stirred for 1 minute. A prescribed amount of the mixture was filled in a metal pan to obtain a cake type foundation.

Evaluation of these compositions were carried out as follows.

(1) SPF

Light source:	Toshiba FL20S.E-30	3 lamps
	central wavelength	306 nm
	distance between light source and irradiated site	60 cm
Irradiation site:	the back of Japanese adult men and women having fair skin and average skin, respectively	
Amount of application:	0.2 g/100 cm ²	

Under the above conditions with varying irradiation time from 3 to 60 minutes at a constant light volume, according to the method for measuring SPF prescribed by FDA, the ratio of minimal erythema dose (MED) at a non-applied site and that of an applied site was calculated from the following formula:

$$SPF \text{ value} = \frac{MED \text{ at the applied site}}{MED \text{ at the non-applied site}}$$

Propriety of the value determined was confirmed by the standard sunscreen (8% homosalat lotion) of FDA method 20 or more).

(2) Transparency

Ten panelists evaluated whether a white tint was observed or not when the creams were spread on the skin according to the following criteria.

- A: All the ten panelists did not observe a white tint.
B: One to five panelists observed a white tint.
C: Six to nine panelists observed a white tint.

(3) Blooming

Ten panelists evaluated whether blooming (a blue tint) was observed or not when the creams were spread on the skin according to the following criteria.

- A: All the ten panelists did not observe a blue tint.
B: One to five panelists observed a blue tint.
C: Six to nine panelists observed a blue tint.

(4) Stability

After preparation of the creams, they were allowed to stand at 50° C. for one week and the existence of agglomerate (grain) was observed according to the following criteria.

- A: No grain was observed.
B: Grain was slightly observed.
C: Grain was clearly observed.

(5) Dispersibility

After preparation of the cake type foundation by pressing, the existence of uneven lump (fine particles of titanium dioxide) was observed according to the following criteria.

- A: No uneven lump was observed.
B: Uneven lump was slightly observed.
C: Uneven lump was clearly observed.

(6) Difference in tint

Ten panelists evaluated a tint of the cake type foundation itself in comparison with that after spread on the skin according to the following criteria.

- A: Nine or ten panelists did not observed any difference in a tint.
B: Two to five panelists observed difference in a tint.
C: Six to eight panelists observed difference in a tint.

The difference in a tint is often observed in a cosmetic containing a conventional finely granulated titanium dioxide particles.

(7) Finish

The cake type foundation was applied on the skin with water. Whitening (such a phenomenon that powder applied was agglomerated and concentrated about the applied site to whiten) or unevenness of finish were evaluated according to the following criteria.

- A: No whitening
B: Slight whitening (or powdery finish)
C: Whitening (or unevenness)

TABLE 1

Runs	Amount of titanium dioxide/[I] or [II] (%)	SPF value	Transparency	Blooming	Stability
Reference	[II] 4%	10.0	1-2	A	A
		30.0	2	A	B
		50.0	3	B	B
		70.0	3	B	C
		10.0	1-2	A	A
Present invention	[I] 4%	30.0	2	A	A
		50.0	3	B	A
		70.0	3	C	A
		0	1	A	A
		10.0	1-2	A	A

TABLE 1-continued

Runs	Amount of [I] or [II]	Titanium dioxide/[I] or [II] (%)	SPF value	Transpar- ency	Blooming	Stability
Present invention	[I] 20%	0.5	1	A	A	A
		1.0	1-2	A	A	B
		5.0	2	A	A	B
		10.0	3	B	B	C
		30.0	8	C	C	C
		0.5	1	A	A	A
		1.0	1-2	A	A	A
		5.0	3	A	A	A
		10.0	4	A	A	A
		30.0	8	B	A	A

TABLE 2

Runs	Amount of [I] or [II]	Titanium dioxide/[I] or [II] (%)	SPF value	Dispersi- bility	Difference in tint	Finish
Reference	[II] 10%	10.0	4	A	B	A
		30.0	7	B	B	A
		50.0	9	B	C	B
		70.0	12	C	C	C
Present invention	[I] 10%	10.0	4	A	A	A
		30.0	7	A	A	A
		50.0	9	A	A	A
		70.0	11	A	A	B
Reference	[II] 50%	0	3	A	A	A
		0.5	3	A	A	A
		1.0	4	A	B	B
		5.0	6	B	B	B
		10.0	9	B	C	C
		30.0	>15	C	C	C
Present invention	[I] 50%	0.5	3	A	A	A
		1.0	4	A	A	A
		5.0	7	A	A	A
		10.0	10	A	A	A
		30.0	>15	A	A	A

As is seen from Tables 1 and 2, the kaolin particles coated with titanium dioxide can be formulated in a cosmetic composition in a wider range in comparison with a mere mixture of a conventional finely granulated titanium dioxide particles and kaolin. Further, the cosmetic composition containing the kaolin particles coated with titanium dioxide shows excellent ultraviolet rays screening effect and preferred cosmetic properties.

The amount of titanium dioxide to coat kaolin is preferably 1 to 50%. When the amount is less than 1%, ultraviolet rays screening effect can hardly be expected and, when the amount is more than 50%, cosmetic properties are impaired.

The kaolin particles coated with titanium dioxide can be formulated in a cosmetic composition of the present invention in an amount of not more than 90% by weight depending upon a type of cosmetics, usually, 90 to 1% by weight. Further, in the cosmetic composition of the present invention, a conventional finely granulated titanium dioxide particles can be formulated in an amount not more than 3% by weight.

The cosmetic composition of the present invention can be prepared in the form of, for example, a cake type or milky lotion type foundation, face powder, lipstick, milky lotion, cream and the like by incorporating the kaolin particles coated with titanium dioxide particles with other conventional cosmetic ingredients such as talc, iron oxides, liquid paraffin, solid paraffin, lanolin, sorbitan sesquioleate, beeswax, stearic acid, distilled water, sodium carboxymethyl cellulose, triethanol amine, propylene glycol and so on according to a conventional method. The other cosmetic ingredients are not limited to a specific one and they can be appropri-

ately chosen according to a desired form and properties of the composition.

The following Examples further illustrate the present invention in detail but are not to be construed to limit the scope thereof.

EXAMPLE 1

A cake type foundation of the following formulation was prepared according to a conventional method.

	Amount (%)
Ingredient A	
Kaolin particles coated with titanium dioxide (amount of coat: 10%)	50.0
Fine particulate titanium dioxide (average particle size 8 μ m)	3.0
Talc	29.3
Red oxide of iron	0.6
Yellow oxide of iron	1.5
Black oxide of iron	0.15
Ingredient B	
Liquid paraffin	8.5
Isopropyl palmitate	1.0
Sorbitan sesquioleate	3.0
Propylene glycol	2.5
Paraben	0.2
Ingredient C	
Perfume	0.25

The ingredients of A were mixed with Henschel mixer for 5 minutes. To the mixture were added dropwise with stirring the ingredients of B previously molten by heating at 70° C. in a separate vessel. Then, the ingredient of C was added and the mixture was stirred

for 1 minute. A prescribed amount of the resulting mixture was filled in a metal pan to obtain a cake type foundation.

In the preparation of the foundation, titanium dioxide was uniformly dispersed and, upon using, it could be uniformly applied on the skin to give very good finish.

EXAMPLE 2

A milky lotion type foundation of the following formulation was prepared according to a conventional method.

	Amount (%)
Ingredient A	
Liquid paraffin	4.0
Glyceryl monostearate	2.0
Stearic acid	3.0
Lanolin	2.0
Solid paraffin	0.5
Propylene glycol monostearate	0.5
Propyl p-hydroxybenzoate	0.1
Ingredient B	
Distilled water	57.2
Triethanol amine	1.0
Sodium carboxymethyl cellulose	0.2
Bentonite	0.5
Polyoxyethylene sorbitan monostearate	1.5
Propylene glycol	7.5
Ingredient C	
Kaolin coated with titanium dioxide (amount of coat: 30%)	10.0
Fine particulate titanium dioxide (average particle size: 8 μ)	2.0
Talc	5.0
Red oxide of iron	0.7
Yellow oxide of iron	2.0
Black oxide of iron	0.3

The ingredients of A and B were molten in separate vessels by heating at 80° C., respectively. The ingredients of B was added to the ingredients of A and the mixture was stirred for 10 minutes. The ingredients of C were added, and the mixture was stirred for 15 minutes and cooled to obtain a milky lotion type foundation.

In the preparation of the foundation, titanium dioxide was uniformly dispersed and, upon using, it could be uniformly applied on the skin to give very good finish.

EXAMPLE 3

A face powder of the following formulation was prepared according to a conventional method.

	Amount (%)
Ingredient A	
Kaolin coated with titanium dioxide (amount of coat: 1%)	90.0
Talc	5.0
Yellow oxide of iron	1.5
Red oxide of iron	1.4
Black oxide of iron	0.1
Ingredient B	
Squalane	2.2
Sorbitan sesquiolate	0.5
Ingredient C	
Perfume	0.3

The ingredients of A were mixed with Henschel mixer for 5 minutes. The ingredients of B were uniformly molten in a separate vessel by heating at 70° C. and added dropwise to the ingredients of A with stirring. Further, the ingredient of C was added dropwise and the mixture was stirred for 1 minute. The mixture

was pulverized with an atomizer to obtain a face powder.

In the preparation of the face powder, titanium dioxide was uniformly dispersed and, upon using, it could be uniformly applied on the skin to give very good finish.

EXAMPLE 4

A lipstick of the following formulation was prepared according to a conventional method.

	Amount (%)
Ingredient A	
Kaolin coated with titanium dioxide (amount of coat: 20%)	5.0
Mica powder	5.0
D & C Red No. 7	0.5
D & C Red No. 9	0.5
Ingredient B	
Candelilla wax	7.0
Solid paraffin	7.0
Beeswax	5.0
Carnauba wax	5.0
Castor oil	44.8
Isopropyl myristate	10.0
Ingredient C	
Perfume	0.2

The ingredients of A and a part of castor oil were uniformly kneaded in a molar to obtain a pigment portion. The remaining ingredients of B were molten by heating. The pigment portion was added to the ingredients of B and uniformly dispersed with a homomixer. Further, the ingredient of C was added and uniformly dispersed. The mixture was cast in a mold and quickly cooled. The resulting solid was fixed in a container and framed.

In the preparation of the lipstick, titanium dioxide was uniformly dispersed and, upon using, it could be uniformly applied on the lip to give very good finish.

EXAMPLE 5

A milky lotion of the following formulation was prepared according to a conventional method.

	Amount (%)
Ingredient A	
Stearic acid	3.0
Cetyl alcohol	1.5
Vaseline	5.0
Liquid paraffin	12.0
Polyoxyethylene monooleate (10 EO)	2.5
Ingredient B	
Polyethylene glycol 1500	2.0
Triethanol amine	1.0
Distilled water	71.5
Kaolin coated with titanium dioxide (amount of coat: 50%)	1.0
Ingredient C	
Perfume	0.5

The ingredients of B were uniformly dispersed by heating at 70° C. The ingredients of A were molten by heating at 70° C. and added to the ingredients of B. The mixture was emulsified with a homomixer. After emulsification, the mixture was cooled with stirring to 30° C. to obtain a milky lotion.

In the preparation of the milky lotion, titanium dioxide was uniformly dispersed and was not agglomerated

during storage. Upon using, it could be uniformly applied on the skin to give very good finish.

EXAMPLE 6

A cream of the following formulation was prepared according to a conventional method.

	Amount (%)
<u>Ingredient A</u>	
Solid paraffin	5.0
Beeswax	4.0
Microcrystalline wax	4.0
Vaseline	7.0
Squalane	30.0
Polyoxyethylene sorbitan monolaurate (20 EO)	1.0
Sorbitan sesquioleate	4.0
<u>Ingredient B</u>	
Distilled water	20.0
<u>Ingredient C</u>	
Kaolin coated with titanium dioxide (amount of coat: 5%)	20.0
Talc	5.0

The ingredients of C were uniformly mixed and dispersed in the ingredient of B at 70° C. Separately, the

ingredients of C were molten at 70° C. with heating and to this was added the above prepared mixture. The resulting mixture was emulsified with a homomixer. After emulsification, the mixture was cooled to 30° C.

In the preparation of the cream, titanium dioxide was uniformly dispersed and was not aggregated during storage. Upon using, it could be uniformly applied on the skin to give very good finish.

What is claimed is:

1. A composition comprising kaolin particles having a coating thereon consisting essentially of titanium dioxide, the amount of titanium dioxide coating the kaolin particles being 1 to 50% by weight based on the total weight of said kaolin particles coated with titanium dioxide.

2. A cosmetic composition according to claim 1, wherein the kaolin particles have an average particle size of 0.5 to 30 μm .

3. A cosmetic composition according to claim 1, wherein the kaolin particles coated with titanium dioxide is formulated in an amount of not more than 90% by weight based on the composition.



US005122418A

United States Patent [19]

Nakane et al.

[11] Patent Number: **5,122,418**[45] Date of Patent: **Jun. 16, 1992**[54] **COMPOSITE POWDER AND PRODUCTION PROCESS**

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[21] Appl. No.: 593,537

[22] Filed: Oct. 4, 1990

Related U.S. Application Data

[63] Continuation of Ser. No. 405,702, Sep. 11, 1989, abandoned, which is a continuation of Ser. No. 375,616, May 24, 1989, abandoned, which is a continuation of Ser. No. 939,379, Dec. 8, 1986, abandoned.

[30] **Foreign Application Priority Data**

Dec. 9, 1985 [JP] Japan 60-276505
Jul. 22, 1986 [JP] Japan 61-172499
Nov. 21, 1986 [JP] Japan 61-278374

[51] Int. Cl.³ A61K 6/00

[52] U.S. Cl. 424/401; 424/59; 424/76.2; 424/76.25; 424/489; 424/46; 424/47

[58] Field of Search 424/489, 501, 471, 59, 424/76.2, 76.25, 46, 47

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[57] **ABSTRACT**

A composite powder wherein an organic or inorganic core powder is substantially completely covered with one or more types of organic, inorganic, or metallic powders having an average particle size one-fifth or less of the average particle size of the above core powder by means of mixing and compression. The composite powder may be manufactured by mixing and compressing the above core powder and coating powder using a ball mill or other mixer charged with a ball shaped mixing medium of an average diameter of 5 mm or less. This composite powder may be used in, for example, skin treatment agent, makeup type cosmetics, sunburn preventing cosmetics, deodorants.

5 Claims, 5 Drawing Sheets

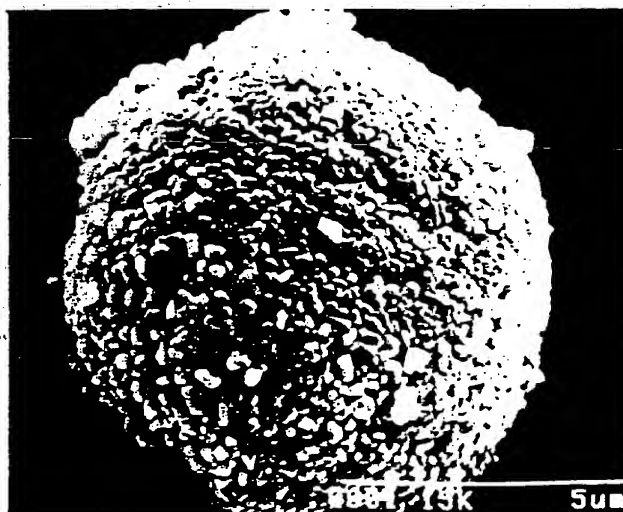


Fig. 1

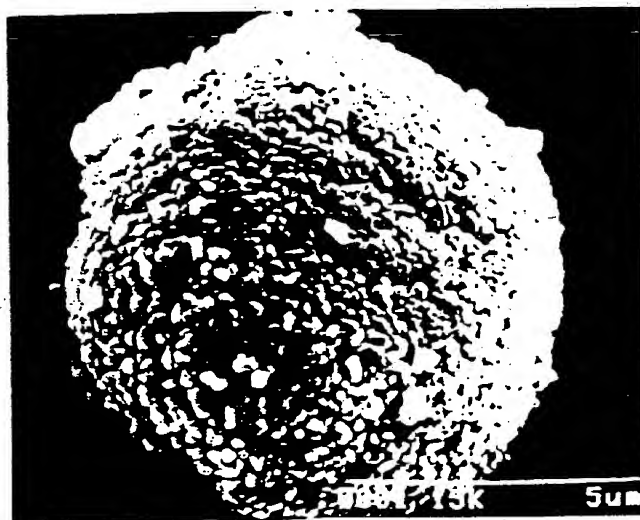


Fig. 2

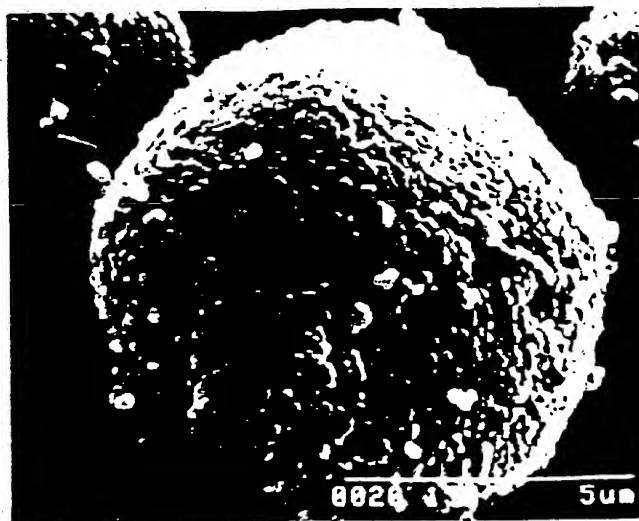


Fig. 3

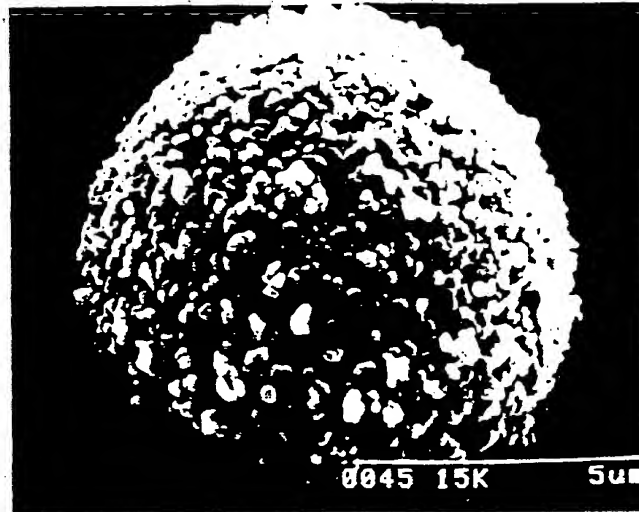


Fig. 4

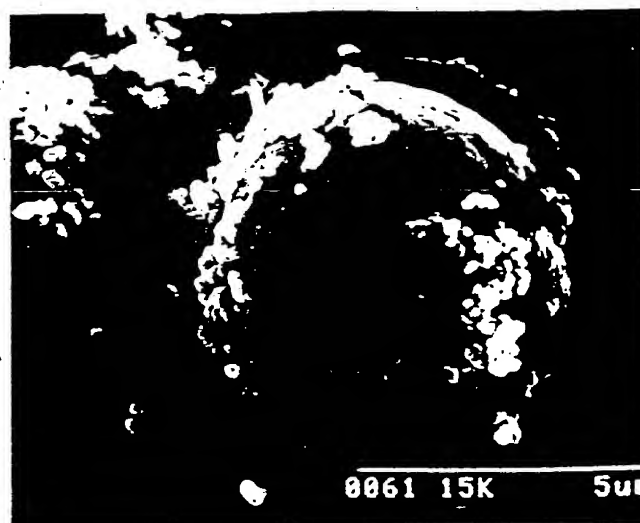


Fig. 5

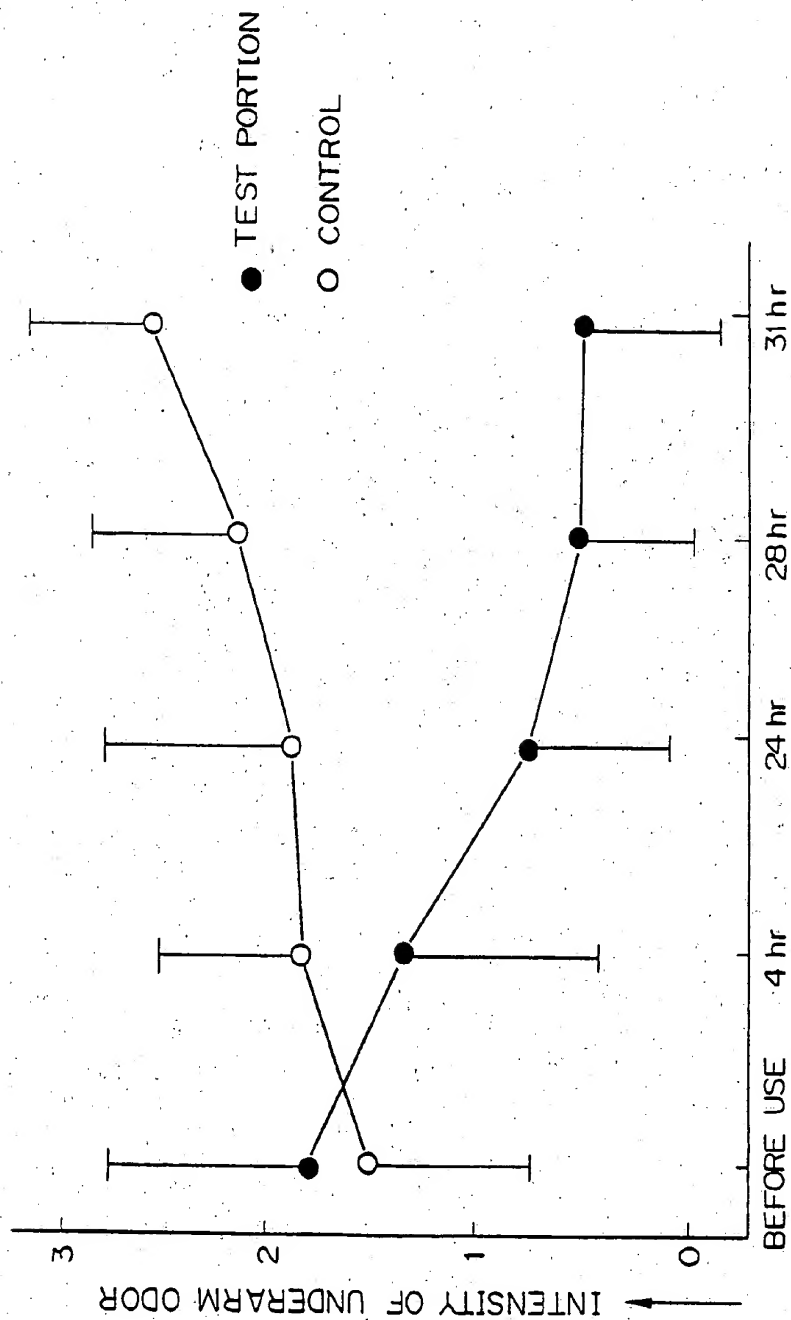
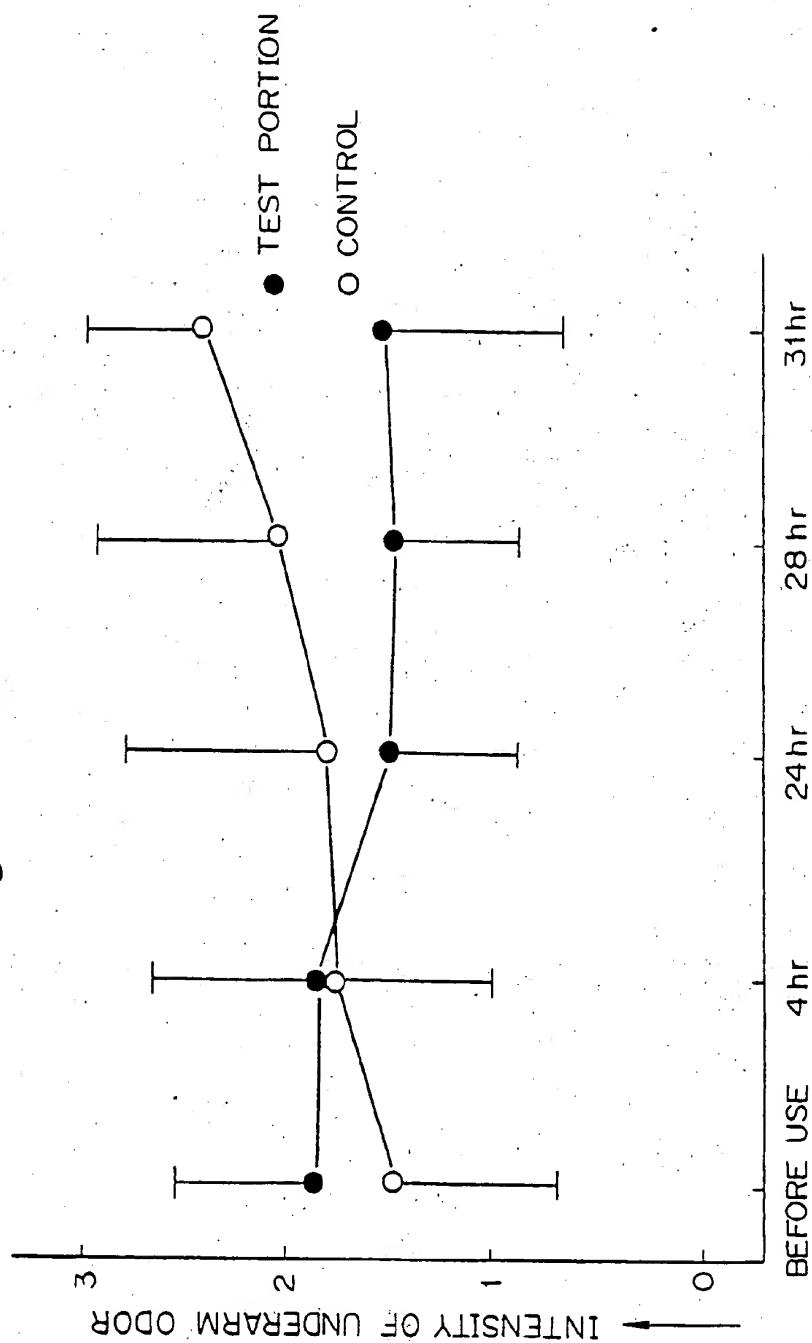
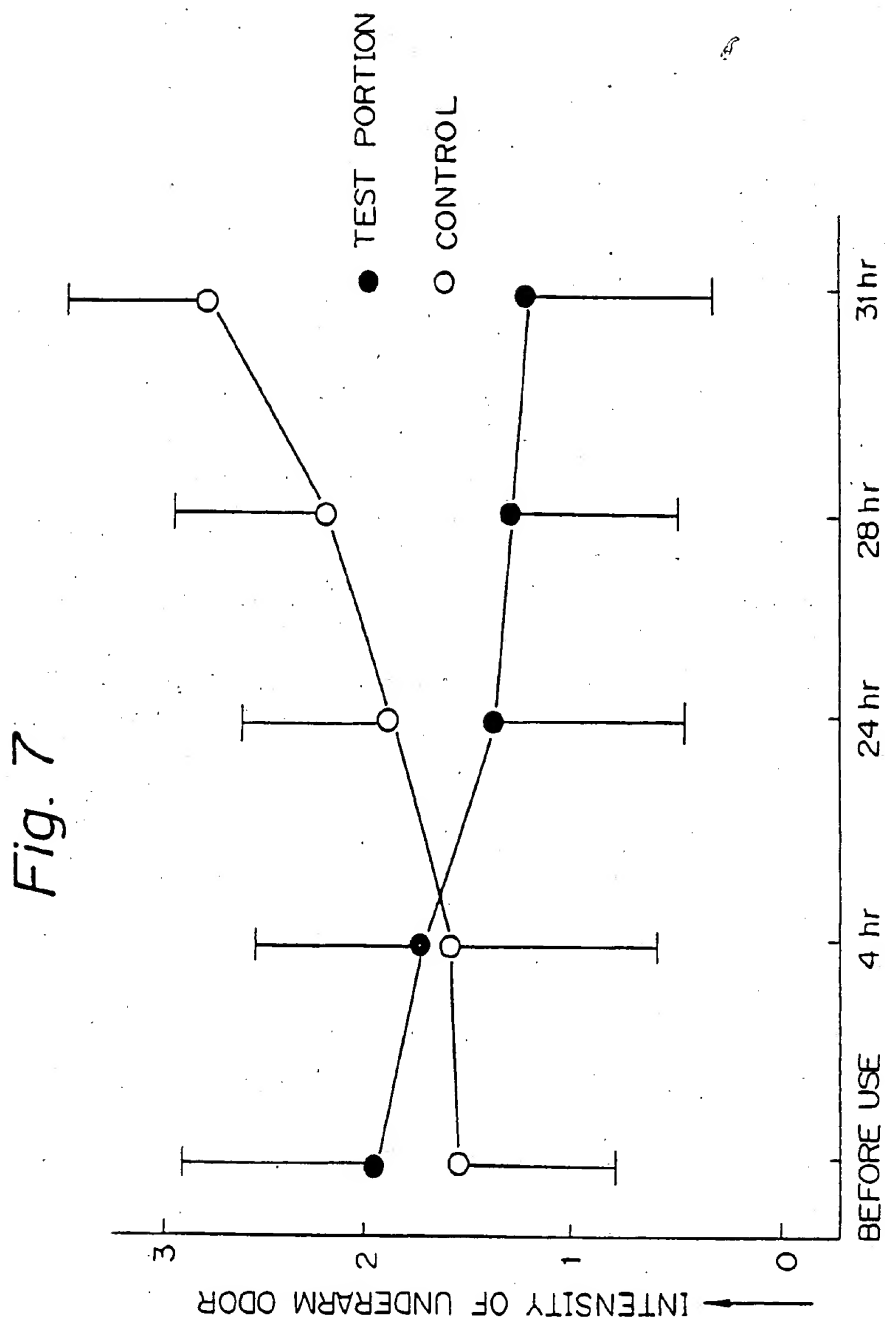


Fig. 6





COMPOSITE POWDER AND PRODUCTION PROCESS

This application is a continuation, of U.S. Ser. No. 405,702 filed Sep. 11, 1989, now abandoned, which is a continuation of application Ser. No. 375,616, filed May 24, 1989, now abandoned, which was a continuation of U.S. application Ser. No. 06/939,379, filed Dec. 8, 1986, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a composite powder wherein the surface of one type of core powder is substantially completely covered with another type of coating powder, thereby improving the surface characteristics of the powder, and a production process and use thereof. More particularly, it relates to a composite powder with a core powder substantially completely covered with a coating powder, and a production process thereof, and a skin treatment agent containing the same, wherein use is made of a ball mill or other continuous or noncontinuous type mixer charged with a ball-shaped mixing medium with an average diameter of 5 mm or less for mixture and compression, one type of organic or inorganic powder being used as the core powder and an organic, inorganic, or metallic powder with an average particle size of one-fifth or less of the average particle size of the core powder being used as the coating powder.

Note that in this specification, "substantially completely covered" means a state wherein the core powder is homogeneously and closely covered by the coating powder. However, when microscopically examining the composite powder formed by substantially completely covering the core powder with the coating powder, it will be seen that there are extremely narrow gaps between the particles of the coating powder.

Further, in this specification, "spherical powder" means any powder from a true spherical shape to an ovoid shape with a long diameter to short diameter ratio of 2:1, and includes slightly deformed powder also.

2. Description of the Related Art

In the prior art, use has been made of ball mills, automated mortars, automatic mortars, and the like to mix and pulverize nylon powder, polymethylmetacrylate powder, and other types of plastic powder and organic powders, titanium dioxide, red oxide, and other inorganic powders by the wet or dry method so as to produce composite powder. However, in the above methods used in the prior art, there are many unsolved problems, such as nonuniformity of the coating, deformation of the core powder, and separation of the coating powder, which detract from the stability of the composite powder.

Conventional cosmetics for use in treating rough skin are prepared with due consideration to the components contained in the secretions of the skin and the components contained in the skin so as to assist the action of the skin by adding moisture retaining components or oils and supplementing components in the skin, thereby maintaining the skin in its normal state or improving it. Further, medicines with an antioxidation function have been added to reduce the products of decomposition of sebum which have a detrimental effect on the skin. However, these effects are still unsatisfactory. Among the skin treatment agents, there are those including

medicines with a skin activation or skin inflammation suppression effect, but stabilization of these is difficult and there are limits to the amount of such medicines which can be compounded.

The inventors engaged in in-depth research for an effective method of maintaining the skin in its normal state and preventing or improving rough skin. As a result, they discovered that it was effective to remove from the sebum components the old waste products of the skin, which have a detrimental effect on the skin. For this purpose, they found that hydroxyapatite powder was superior in selective adsorption of the old waste products of sebum, i.e., free fatty acids and liquid peroxide, and was effective for the prevention of rough skin, improving rough skin, and suppression of skin inflammation of patients suffering from acne. However, if hydroxyapatite powder is compounded in a skin treatment agent as it is, the hydroxyapatite powder would not sufficiently spread over the skin since it has a strong agglomeration property, so the problem remained that the full effect of the adsorption of the decomposed sebum could not be enjoyed.

On the other hand, makeup type cosmetics are usually produced with the inclusion of some oils, wax, hydrocarbons, higher alcohols, and other oil components, powders, coloring matter, and other components, e.g., antioxidants, plasticizers, and solvents. Such makeup type cosmetics have been given a better feel, i.e., a better smoothness and easier applicability, by the addition of spherical powder. However, polyamide resin, polyethylene resin, methyl methacrylate resin, cellulose resin, polystyrene resin, polypropylene resin, styrene and acrylate copolymers, and other organic spherical powder, silica, alumina, magnesium carbonate, and other inorganic spherical powder can impart to makeup type cosmetics the desired feel, i.e., excellent smoothness and easy applicability, because the particles thereof are spherical in shape, but the spherical powders have a low index of refraction, so are poor in hiding power. Therefore, if these spherical powders are compounded in makeup type cosmetics such as foundations, in which a high hiding power is sought, the desired hiding power will not be imparted. When a powder with a high index of refraction is used at the same time to impart the hiding power, a uniform skin covering effect cannot be obtained due to the large difference in hiding powers. This leads to streaking and blotching and thus detracts considerably from the beauty of the finish when applying foundation to the skin. Further, the afore-mentioned spherical powder is a low refractive index powder, and when used together with coloring agents, the problems arise of uneven color, color separation, and color streaking and blotching, from which point also there is a significant detracting from the stability of the product and the beauty of the finish upon application. The same problems of uneven color, color separation, and color streaking and blotching occur in compounding a spherical powder having a high index of refraction, such as titanium dioxide.

Further, it is known in the art to use a ball mill, automated mortar, automatic mortar, etc. to mix and pulverize, by the wet method or dry method, spherical nylon powder, spherical polymethylmetacrylate powder, and titanium dioxide, red iron oxide, and other inorganic powders to produce a composite powder, but the prior art products have featured a nonuniform covering of the coating powder, i.e., not a substantially complete covering, and a slight mechanical force was sufficient to

cause an easy separation of the coating powder. The coating powder would also separate easily in oils or solvents. Thus, the problem remains that the stability of the composite powder is not sufficient. Composite powders suffering from such problems have the disadvantage that, due to the nonuniformity of the covering of the coating powder on the spherical core powder, first, the shape of the powder becomes significantly different from the spherical shape, so the powder cannot impart an excellent smoothness and easy applicability to makeup type cosmetics. Second, when a spherical powder having a low index of refraction is covered with a white coating powder, portions with no hiding power are exposed, and thus the hiding power given to the makeup type cosmetic is insufficient or differences in the hiding power arise, leading to streaks and blotching and significantly detracting from the beauty of the finish upon application to the skin. Also, when the coating powder is a colored powder, uncolored portions are exposed, leading to uneven color, color separation, and color streaking and blotches, similarly significantly detracting from the beauty of the finish. Third, even when a high index of refraction spherical powder is covered with a colored powder, similar problems arise as when covering a low index of refraction spherical powder by a colored powder.

Note, it is known that the ultraviolet rays in sunlight causes acute inflammation of the skin upon overexposure to the same, and long-term exposure causes early aging of the skin, pigmentation, and wrinkles and is a factor behind skin cancer. Therefore, as the effects of ultraviolet rays on the skin have become clearer, the demand for sunburn preventing cosmetics which protect the skin from ultraviolet rays has been rising.

Sunburn preventing cosmetics contain ultraviolet absorbers or ultraviolet scatterers for blocking the ultraviolet rays. Known ultraviolet absorbers include benzophenones, cinnamic acids, benzoic acids, etc. These have a narrow ultraviolet absorption band in most cases and cannot necessarily be said to have a satisfactory blockage of a wide range of ultraviolet rays. Also, they interact with the other components of the cosmetic, and thus degrade the stability of the product or, when a larger amount is compounded so as to raise the ultraviolet absorption effect, cause problems in terms of skin safety. Therefore, to block a wide range of ultraviolet rays, use is made of ultraviolet scatterers. As ultraviolet scatterers, use is made of zinc oxide, titanium oxide, kaolin, calcium carbonate, and other inorganic pigments. However, while inorganic pigments displaying such ultraviolet scattering effects have a high skin safety and effectively scatter a wide spectrum of ultraviolet rays, when compounded in cosmetics, they enter into an agglomerated state known as secondary agglomeration, and thus a large amount must be compounded to give a sufficient ultraviolet scattering effect. In such a case, the hiding power becomes too great, and thus, when the cosmetic is applied to the skin, it appears too heavy, resulting in the problem of an unnatural finish. A similar art to the present invention is Japanese Unexamined Patent Publication (Kokai) No. 61-194013, entitled "Sunburn Preventing Cosmetic". In that publication, disclosure is made of the use of particles of an insoluble polymer compound to which titanium oxide is adhered. The covering power of the titanium oxide is too high, however, and has a hiding power six to seven times that of zinc oxide. Therefore, when compounded with the

aim of raising the ultraviolet scattering effect, the result is again a too heavy makeup appearance.

Further, in Japanese Unexamined Patent Publication (Kokai) No. 60-231607, entitled "Sunburn Preventing Cosmetic", disclosure is made of compounding zinc oxide with an average particle size of 10 to 60 microns so as to give a sunburn prevention effect. When zinc oxide is compounded in a cosmetic, however, secondary agglomeration occurs, and thus a sufficient sunburn preventing action cannot be expected. Further, there is the problem in that the applicability, in particular the feel of use as a cosmetic, deteriorates.

On still another matter, underarm odor, sweat odor, foot odor, hair odor, menstrual odor, and other body odors are frequently explained as deriving from the bacterial decomposition of sweat (for example, see Labows, Kligman, et al, J. Soc. Cosmet. Chem., 34, 1982, page 193). Numerous products are on the market for dealing with such odors. Most of these products include sweat repressants, bactericides, masking agents, and absorbents. Almost all suppressants which reduce the amount of sweat are astringent aluminum compounds. Usually, use is made of aluminum hydroxychloride. On the other hand, as the bactericide for the prevention of a proliferation of bacteria, the cause behind odors, use is often made of hexachlorophene and various quaternary aluminum compounds. Further, as masking agents, use is made of eugenol and other substances having a pleasant odor. These sweat suppressants, bactericides, and masking agents are currently compounded singly or in free combination in products.

However, sweat suppressants act to reduce the source of the sweat odor, the sweat, but complete suppression of sweat is not possible from a biological viewpoint. Considering the action mechanism, further, there is a defect that it is not possible to suppress an already occurring sweat odor.

On the other hand, safety problems have been pointed out for bactericides, which prevent a proliferation of bacteria which break down the sweat and thus lead to the odors. It is not possible to compound them in concentrations enabling a sufficient effect.

Further, masking agents mix with the sweat odors and sometimes, conversely, give rise to an unpleasant smell.

Therefore, conventional deodorants containing sweat suppressors, bactericides, and masking agents suffer from unsatisfactory effectiveness, safety, and practicality in use.

SUMMARY OF THE INVENTION

Accordingly, the objects of the present invention are to eliminate the above-mentioned disadvantages of the prior art and to provide a composite powder in which the surface of core powder is substantially completely covered by a coating powder and deformation of the core powder is minimized.

Another object of the present invention is to provide a process for producing the above-mentioned composite powder.

Still another object of the present invention is to provide a skin treatment agent having a superior adsorption to prior skin waste products.

Still another object of the present invention is to provide a makeup type cosmetic wherein the organic or inorganic spherical powder does not impair the excellent smoothness and easy applicability imparted during practical use of the makeup cosmetic, the spherical core

powder is uniformly covered by the coating powder, the coating powder does not separate therefrom no matter what production process the makeup cosmetic passes through, the functionality of the coating powder on the spherical core powder can be imparted in a complete fashion, the hiding power is sufficient, and upon application to the skin, streaking or blotching, uneven color, and color separation can be suppressed, thus giving a beautiful finish.

Still another object of the present invention is to provide a sunburn preventing cosmetic which, in the case of compounding a zinc oxide covering resin powder in the sunburn preventing cosmetic, has a suitable hiding power and gives a natural finish, and exhibits a sufficient ultraviolet scattering ability.

Still another object of the present invention is to provide a deodorant which uses a composite powder comprised of a synthetic resin powder and hydroxyapatite as the active deodorizing ingredient and which is superior in terms of efficacy, safety, and practical use.

Other objects and advantages of the present invention will be apparent from the following description.

In accordance with the present invention, there is provided a composite powder wherein an organic or inorganic core powder is substantially completely covered with one or more types of organic, inorganic, or metallic powders having an average particle size one-fifth or less of the average particle size of the above core powder by means of mixing and compression. The composite powder may be manufactured by mixing and compressing the above core powder and coating powder using a ball mill or other mixer charged with a ball shaped mixing medium having an average diameter of 5 mm or less, thus enabling a composite powder with a uniform particle size and covering and extremely little deformation.

In accordance with the present invention, there is also provided a skin treatment agent wherein an organic or inorganic spherical composite powder having an average particle size of 1 to 100 microns is used as the core powder and hydroxyapatite powder having an average particle size one-fifth or less of the average particle size of the above core powder is used as the coating powder, and they are mixed and compressed so that the spherical core powder is substantially completely covered by the coating powder to form a spherical composite powder which is compounded into the agent. The skin treatment agent is superior to skin treatment agents in which the hydroxyapatite powder is compounded in its original state, in that it has a good feeling during application and is more effective in preventing rough skin, improving rough skin, and suppressing inflammation of the skin for sufferers of acne.

In accordance with the present invention, there is further provided a makeup type cosmetic wherein an organic or inorganic spherical powder having an average particle size of 1 to 100 microns is used as the core powder and one or more types of an organic, inorganic, or metallic powder having an average particle size one-fifth or less of the average particle size of the above core powder is used as the coating powder, and they are mixed and compressed so that the spherical core powder is substantially completely covered by the coating powder to form a spherical composite powder which is compounded into the cosmetic.

In accordance with the present invention, there is still further provided a sunburn preventing cosmetic containing a resin powder covered on the surface thereof

with zinc oxide alone or one or more of zinc oxide and another inorganic powder.

In accordance with the present invention, there is still further provided a deodorant which uses a composite powder consisting of a resin powder and one or more of hydroxyapatite, metal oxides, and halogen compounds as a deodorizing active ingredient. The deodorant can be used in the form of, for example, aerosols, roll-ons, powders, lotions, creams, sticks, and other external deodorants, and further, shoe lining and household use type deodorants.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be better understood from the description set forth below with reference to the accompanying drawings, in which:

FIG. 1 is an electron micrograph (10000 magnifications) showing the particle structure of the composite powder obtained in Example 1;

FIG. 2 is an electron micrograph (10000 magnifications) showing the particle structure of the composite powder obtained in Example 1 after colloid milling;

FIG. 3 is an electron micrograph (10000 magnifications) showing the particle structure of the composite powder obtained in Comparative Example 1;

FIG. 4 is an electron micrograph (10000 magnifications) showing the particle structure of the composite powder obtained in Comparative Example 1 after colloid milling;

FIG. 5 shows the effects of an aerosol type deodorant spray in Example 30;

FIG. 6 is a graph showing the changes with time in the strength of the underarm odor of a test portion and control portion in an actual usage test employing an aerosol deodorant spray wherein the composite powder in the deodorant spray of Example 30 is replaced with nylon; and

FIG. 7 is a graph showing the changes with time in the strength of the underarm odor with a deodorant spray of Example 30 wherein the composite powder is replaced with zinc oxide.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the manufacture of the composite powder according to the present invention, it is most effective to use a substantially spherical powder as the core powder. By making the mixing medium of the apparatus (mixer) used for the mixing and pulverization of conventional solids and the core powder smaller, the effect of mixing and compressing can be optimized. The idea that conventional spherical matter could be mixed and pulverized while maintaining its spherical shape had not been conceived, even by persons skilled in the art. According to the method of the present invention, use is made of spherical powder not considered at all in the prior art, as the core powder, and the surface thereof is substantially completely covered by a coating powder having an average particle size one-fifth or less of the average particle size of the core powder. This is an epochmaking development in view of the standard thinking in the prior art.

As the core powder and the coating powder constituting the composite powder of the present invention, use may be made of any organic or inorganic powder. Representative examples include polyamide resin, polyethylene resin, acrylic resin, polyester resin, fluorine resin, cellulose resin, and other organic powder and

titanium dioxide, talc, kaolinite, zinc white, magnesium oxide, calcium oxide, barium sulfate, magnesium carbonate, calcium carbonate, silica, calcium secondary phosphate, iron oxide, chromium oxide, chromium hydroxide, ultramarine blue, prussian blue, hydroxyapatite, and other inorganic powder, or silicon treated, activant treated, wax treated or other treated powder of the same. Any one of these can be used as the core powder. One or more of the above organic or inorganic powder or aluminum powder, gold powder, silver powder, iron powder, or other metallic powders or halogen compounds can be used as the coating powder. There is no particular limitation to the combination of the core powder and coating powder—an organic powder and organic powder, organic powder and inorganic powder, organic powder and metallic powder, inorganic powder and organic powder, inorganic powder and inorganic powder, or inorganic powder and metallic powder—are all acceptable. However, the average particle size of the coating powder with respect to the average particle size of the core powder must be one-fifth or less, preferably one-tenth or less. If the average particle size of the coating powder is greater than one-fifth of that of the core powder, the stability, i.e., non-separation, of the coating powder deteriorates considerably.

The average particle size of the core powder of the composite powder according to the present invention is usually 1 to 100 microns, preferably 3 to 30 microns. As the coating powder, use may be made of resin powder, silica, alumina, magnesium carbonate, talc, kaolinite, mica, and other white colored low index of refraction powders. Even if the index of refraction is low, the hiding power increases in accordance with the reduction of the particle size (until a size of one-half or less of the wavelength of visible light), and thus, with a powder having an average particle size one-fifth or less the size of the core powder, the hiding power of the core powder can be increased, and accordingly, the object of the invention achieved. As the method for manufacturing the composite powder to be compounded in cosmetics in the present invention, an organic or inorganic powder for use as the spherical core powder and one or more types of an organic, inorganic, or metallic powder of an average particle size one-fifth or less the average particle size of the spherical core powder for use as the coating powder are mixed and pulverized, using a continuous or noncontinuous type mixer charged with a ball shaped mixing medium of an average size of 5 mm or less, thereby enabling the core powder to be substantially completely covered by the coating powder. The spherical composite powder obtained by this method of manufacture differs from the conventional powder in that the particle size and the covering are uniform and there is very little deformation.

As the mixer used for the manufacture of the spherical composite powder used in the present invention, mention may be made of a tumbling mill, vibration ball mill, satellite ball mill, sand mill, attriter, or any other mixer. Any of these may be used optimally. However, these mixers conventionally used balls of an average size of 30 mm or less as the mixing medium, and when such a ball mill is used, the core powder and coating powder are sometimes pulverized and deformed and the frequency of contact with the powder is low, so it is sometimes impossible to manufacture a composite powder with the core powder completely covered by the coating powder. Therefore, the ball shaped mixing me-

dium used for the manufacture of the spherical composite powder must be one with an average size of 5 mm or less, preferably, from the viewpoint of good workability, 2 to 5 mm.

As mentioned above, if the ball shaped mixing medium is larger than 5 mm in average size, the core powder cannot be substantially completely covered or deformation or pulverization of the powder will occur, and this is not preferable. There is no particular limitation to the materials of the ball shaped mixing medium of the mixer used in the manufacture of the spherical composite powder: ceramic, metal, or plastic materials may all be used.

There is no particular limitation between the amount of powder and the amount of mixing medium of the mixer in the manufacture of the spherical composite powder, but generally speaking, the larger the amount of mixing medium vis-a-vis the amount of powder, the greater the mixing and compressing effect, and thus the faster the processing is completed, but this in turn readily invites deformation of the spherical composite powder. Further, the lower the amount of mixing medium, the smaller the compressing effect and the longer the processing, but the lower the deformation of the spherical composite powder. Therefore, preferably the amount of mixing medium used is 300 to 700 parts by weight to 100 parts of the overall powder.

In the manufacture of the above-mentioned spherical composite powder, there must be a top open space inside the mixer when the ball-shaped mixing medium is charged therein. A top open space of one-third to two-thirds is preferable.

The temperature of the mixer during processing is not critical so long as it does not impair the properties and shape of the powder used.

Further, the atmosphere in the top open space of the mixture during the processing is not critical. Note that it is preferable to mix the core powder and the coating powder with a Henschel mixer or other general powder mixer before the mixing and compressing treatment. Further, concurrent use may be made of water, alcohol, or other liquids in the powder under treatment by the mixer in the working of the present invention.

As mentioned above, in the manufacture of the composite powder, use is made in the mixer of a ball shaped mixing medium of an average size of 5 mm or less, whereby it is possible to suppress to a minimum the pulverizing effect on the powder and to strikingly increase the frequency of contact, and thus promote a strong bonding of the coating powder adhered to the surface of the core powder by static electricity, etc., which enables the manufacture of a composite powder with a uniform particle size, with the core powder substantially completely covered by the coating powder, and with a superior stability against separation.

Spherical core powder is also used for the spherical composite powder compounded into the makeup type cosmetic of the present invention. In the art of manufacture of such a composite powder, it is most effective to use powder of a substantially spherical shape as the core powder. By making the mixing medium of the apparatus (mixer) used for the mixing and pulverization of conventional solids and the core powder smaller, it is possible to optimize the effect of the mixing and compression. The idea that conventional spherical matter could be mixed and pulverized while maintaining its spherical shape had not been conceived by persons skilled in the art. According to the method of the present invention,

use is made of a spherical powder, not considered at all in the prior art, as the core powder, and its surface substantially completely covered by coating powder having an average particle size one-fifth or less of the average particle size of the core powder. This is an epochmaking development in view of the standard thinking in the prior art.

The minimum amount of coating powder required for manufacture of the spherical composite powder according to the present invention is that which will completely cover the core powder in a single particle layer.

"Hydroxyapatite", which is compounded in the skin treatment agent of the present invention, is a mineral name. The mineral is expressed in chemical formula as $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. It is known as an inorganic component of the bones of vertebrates. Almost all of the naturally produced apatite minerals are fluoro apatite, i.e., $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, since the hydroxyapatite powder is usually synthesized by the wet or dry method as mentioned below. As an example of the wet method, calcium hydroxide and phosphoric acid are reacted in an aqueous solution at a temperature from room temperature to about 60° C. to obtain hydroxyapatite powder. On the other hand, as an example of the dry method, calcium carbonate and calcium phosphate are solid phase reacted in air or in a steam atmosphere at a high temperature of 900° C. to 1200° C. to obtain the hydroxyapatite. When a fine particle form of hydroxyapatite powder is required, the wet method is preferable.

The average particle size of the hydroxyapatite must be one-fifth or less, preferably one-tenth or less, of the average particle size of the core powder. If the average particle size of the hydroxyapatite is larger than one-fifth that of the core powder, the stability of the hydroxyapatite against separation will decline considerably, which is not preferable.

The skin treatment agent of the present invention may contain, in addition to the above-mentioned composite powder, cosmetics, pharmaceuticals, quasi-drugs, and other components in general use.

For example, it may also contain talc, kaolinite, mica, sericite, muscovite, phlogophite, synthetic mica, lepidolite, biotite, lithia mica, vermiculite, magnesium carbonate, calcium carbonate, diatomaceous earth, magnesium silicate, calcium silicate, aluminum silicate, barium silicate, barium sulfate, strontium silicate, metal salts of tungstate, silica, zeolite, boron nitride, ceramic powder, and other inorganic powder, nylon powder, polyethylene powder, benzoguanamine powder, tetrafluoroethylene powder, fine crystalline cellulose, and other organic powder, titanium oxide, zinc oxide, and other inorganic white pigments, iron oxide (red iron oxide), iron titanate, and other inorganic red pigments, gamma-iron oxide, and other inorganic brown pigments, yellow iron oxide, yellow ochre, and other inorganic yellow pigments, black iron oxide, carbon black, and other inorganic black pigments, manganese violet, cobalt violet, and other inorganic purple pigments, chromium oxide, chromium hydroxide, cobalt titanate, and other inorganic green pigments, ultramarine blue, prussian blue, and other inorganic blue pigments, titanium oxide coated mica, titanium oxide coated bismuth oxychloride, bismuth oxychloride, titanium oxide coated talc, guanine, colored titanium oxide coated mica, and other nacreous pigments, aluminum powder, copper powder, and other metal powder dyes, C.I. 15850, C.I. 15585, C.I. 15630, C.I. 15880, C.I. 73360, C.I. 12085, C.I. 15865, C.I. 12075, C.I. 21110, C.I. 15510, C.I. 11680,

C.I. 74160, C.I. 45430, C.I. 45410, C.I. 45100, C.I. 17200, C.I. 45380, C.I. 45190, C.I. 12140, C.I. 15510, C.I. 19140, C.I. 15985, C.I. 45350, C.I. 47005, C.I. 42053, C.I. 42090, zirconium, barium or aluminum lake organic pigments, chlorophyll, betacarotene, and other natural colors, squalane, liquid paraffin, vaseline, microcrystalline wax, ozocerite, ceresine, cetyl alcohol, hexadecyl alcohol, oleyl alcohol, cetyl-2-ethylhexanoate, 2-ethylhexylpalmitate, 2-octyldecylmyristate, 2-octyldodecyl gum ester, neopentyl glycol-2-ethylhexanoate, glyceryl triisostearate, 2-octyldodecyl oleate, isopropylmyristate, glyceryl triisostearate, coconut oil fatty acid triglyceride, olive oil, avocado oil, lanolin, dimethylpolysiloxane, and other hydrocarbons, oils and fats, esters, higher alcohols, waxes, silicone oil, and other oils, ultraviolet absorbents, antioxidants, preservatives, surfactants, moisture retainers, perfumes, water, alcohol, and thickening agents.

The zinc oxide used in the sunburn preventing cosmetics of the present invention may be any in general use for cosmetics, but in general has an average particle size of 0.01 to 1 micron, preferably 0.01 to 0.1 micron.

The resin powder referred to in the present invention preferably includes polyester, polyethylene, polystyrene, polymethyl methacrylate, cellulose, chitin, chitosan, 12 nylon, 6 nylon, epoxy resin, acrylic resin, methacrylic resin, teflon, polyvinyl chloride. The resin powder may be spherical or amorphous in shape and may be porous or nonporous. The powder used is one with an average particle size of 1 to 100 microns or so, and is selected so that the average particle size of the zinc oxide is in a range of 1/1000 to 1/5 the average particle size of the resin powder.

In the manufacture of the zinc oxide covered resin powder of the present invention, zinc oxide and resin powder are mixed by the wet or dry method, for example. As the mixer, various ball mills, pot mills, automated mortars, automatic mortars, attriters, etc. may be appropriately used.

The ratio of amounts used when mixing the zinc oxide and resin powder should be 0.1 to 200 parts of zinc oxide to 100 parts of resin powder.

At this time, as the powder adhered to the resin powder, use may be made, in addition to the zinc oxide, of other inorganic powder, for example, talc, mica, titanium oxide, kaolinite, chrome oxide, yellow iron oxide, red iron oxide, black iron oxide, barium sulfate, prussian blue, ultramarine blue, aluminum hydroxide, aluminum silicate, silicic acid anhydride, silicic acid hydrate, and the like to an extent wherein the effects of the present invention are not impaired.

The zinc oxide covered resin powder may be compounded in the sunburn preventing cosmetic as it is, or may be subjected first to surface reformation as commonly used for cosmetic powder for improving the dispersion stability and usability, e.g., may be treated with an activator, metallic soap, or silicone.

The amount of the zinc oxide covered resin powder compounded in the sunburn preventing cosmetic should be 0.1 to 60 percent, preferably 0.5 to 20 percent. When less than 0.1 percent, a sufficient ultraviolet scattering effect cannot be expected. When over 60 percent, it is not practical in terms of the feeling during use.

The sunburn preventing cosmetic of the present invention may include, in addition to the above-mentioned essential component, oils, water, surfactants, moisture retainers, thickening agents, perfumes, medicines, antioxidants, chelating agents, colors, preserva-

tives and antibacterial agents, ultraviolet absorbents, and other components usually used in cosmetics in accordance with the application of the product to a quantity and quality that do not impair the effects of the present invention.

The sunburn preventing cosmetic of the present invention may be a powder, cream, paste, stick, lotion, or the like in form and is not restricted to any of the same.

As the resin powder used as a component of the deodorant of the present invention, mention may be made of nylon, polyvinyl alcohol, polyvinyl chloride, polyester, polyethylene, polypropylene, polyvinylidene cyanide, polyurea, polystyrene, polyurethane, polyfluoroethylene, epoxy resin, acrylic resin, methacrylic resin, cellulose, chitin, chitosan, etc. Preferably, nylon, polyethylene, and polypropylene, especially preferably nylon, are used.

The deodorant according to the present invention uses as its active deodorizing ingredient a composite powder constituted of the above-mentioned resin powder and hydroxyapatite; metal oxides such as zinc oxide, magnesium oxide, and calcium oxide; and/or halogen compounds hexachlorophene, benzethonium chloride, aluminum hydroxychloride, aluminum zirconium chlorohydrate, berberine chloride, chlorophyllin-copper complex, sodium copper chlorophyllin, and benzalkonium chloride. Preferably hydroxyapatite, zinc oxide, and aluminum hydroxychloride. These deodorant components may be preferably compounded in the deodorant in an amount 0.1 to 60 percent by weight. As other components of the deodorant, any known component can be used.

As such components, mention may be made of avocado oil, almond oil, olive oil, grapeseed oil, sesame oil, sasanqua oil, safflower oil, soybean oil, camelia oil, corn oil, rapeseed oil, persic oil, castor oil, sunflower oil, cottonseed oil, peanut oil, cocoa oil, palm oil, coconut oil, milkfat, fish oil, hardened oil, turtle oil, hog oil, mink oil, egg yolk oil, and other oils and fats, spermaceti, shellac, bees wax, lanolin, liquid lanolin, carnauba wax, candelilla wax, and other waxes, liquid paraffin, liquid polyisobutylene, squalane, pristane, vaseline, paraffin, ceresine, and other hydrocarbons, ethanol, isopropanol, lauryl alcohol, cetanol, 2-hexyl decanol, stearyl alcohol, isostearyl alcohol, oleyl alcohol, lanolin alcohol, and other alcohols, ethylene glycol, diethylene glycol monoethylether, triethylene glycol, polyethylene glycol, propylene glycol, 1,3-butylene glycol, glycerine, batyl alcohol, and other polyhydric alcohols, glucose, cane sugar, milk sugar, xylitol, sorbitol, mannitol, maltiol, and other sugars, diisopropyl adipate, hexyldecyl isostearate, cetyl isooctate, oleyl oleate, decyl oleate, lanolin acetate, butyl stearate, isopropyl myristate, diethyl phthalate, hexyl laurate, and other esters, aluminum stearate, magnesium stearate, zinc stearate, and other metal soaps, arabic gum, sodium alginate, caseine, carrageenan, karaya gum, agar-agar, quince seed, gelatin, dextrin, starch, tragacanth, pectin, and other natural water soluble polymer compounds, propylene glycol alginate, ethyl cellulose, crystalline cellulose, methyl cellulose, and other semisynthetic polymer compounds, carboxyl vinyl polymers, polyvinyl methyl ethers, methoxyethylene maleic anhydride copolymers, and other synthetic polymer compounds, dialkylsulfosuccinic acid salts, alkylarylsulfonic acid salts, higher alcohol ester sulfate salts, ester phosphate salts, and other surfactants, ethyl parahydroxybenzoate, methyl parahydroxybenzoate, and other preservatives, vitamin

A, vitamin D, vitamin E, vitamin K, and other vitamins, estradiol, ethynylestradiol, cortisone, and other hormones, C.I. 16185, C.I. 42090, C.I. 15850, C.I. 45350, C.I. 59040, C.I. 60725, and other organic colors, aluminum powder, talc, kaolinite, bentonite, mica, titanium-coated mica, red iron oxide, carmine, and other inorganic colors, urocanic acid, cynoxate, and other ultraviolet absorbents, allantoin, aloe powder, guaiazulene, and other inflammation suppressants, Freon 113, Freon 114, Freon C 318, methylchloride, methylene chloride, isobutane, carbonic acid gas, and other propellants, and purified water.

As other additives which can be compounded at will with the deodorant according to the present invention, mention may be made of aluminum hydroxychloride, aluminum chloride, aluminum sulfate, basic aluminum bromide, aluminum phenolsulfonic acid, tannic acid, aluminum naphthalene sulfonic acid, basic aluminum iodide, and other sweat suppressants, 3,4,4-trichlorocarbaniide (TCC), benzalkonium chloride, benzethonium chloride, alkyltrimethylammonium chloride, resorcinol, phenol, sorbic acid, salicylic acid, hexachlorophene, and other bactericides, musk, skatole, lemon oil, lavender oil, absolute, jasmine, vanillin, benzoin, benzyl acetate, menthol, and other masking agents.

The composite powder comprised of the resin powder and hydroxyapatite, compounded as an essential component of the deodorant of the present invention, can be manufactured by any method, but preferably a resin powder is used as the core powder and the core powder is substantially completely covered with hydroxyapatite having an average particle size one-fifth or less of the resin powder.

The ratio of the amount of the resin powder and the coating powder used may be changed arbitrarily depending on the form of the product and is not particularly limited, but preferably the percent by weight of the hydroxyapatite to the resin powder is from 5 to 60 percent. Further, the particle size of the synthetic resin powder is not particularly limited, but is preferably about 0.5 to 20 microns when used for a deodorant applied to the skin, etc.

The composite powder compounded as the active deodorizing ingredient in the deodorant of the present invention can be manufactured by the mixing technique. That is, it is possible to use a tumbling mill, vibration ball mill, satellite ball mill, sand mill, attriter, or any other mixer. Further, if the ball shaped mixing medium of the ball mills etc. used has an average particle size of 5 mm or less, a composite powder can be obtained wherein, for example, the surface of the resin powder is substantially completely covered with hydroxyapatite powder by strong compression, and thus the stability against separation is high (i.e., the hydroxyapatite will not easily separate from the surface of the synthetic resin powder).

According to the present invention, as mentioned above, the surface of the core powder is substantially completely covered by a powder serving as a coating powder, enabling an improvement of the surface characteristics of the core powder. For example, by covering the surface of a spherical core powder with a coating powder having hiding power, a spherical composite powder having an excellent smoothness and hiding power can be made, the surface of a hydrophilic core powder can be covered with a water repellent coating powder to give water repellency, or conversely, the surface of a water repellent core powder can be cov-

ered with a hydrophilic coating powder to give hydrophilicity, the surface of a low specific gravity core powder can be covered with a high specific gravity coating powder to make a low specific gravity powder, the surface of a spherical core powder can be covered with a colored coating powder with a poor smoothness to make a colored composite powder with a good smoothness, and the surface of a nonmagnetic core powder can be covered with a magnetic coating powder to make a magnetic composite powder, etc. Thus a tremendous effect is obtained in that the surface characteristics of all sorts of powders can be improved.

The skin treatment agent of the present invention has a superior feel during application and adsorbs the decomposed sebum, i.e., products of decomposition of triglyceride, that is, free fatty acids, and various liquid peroxides arising due to oxidation deterioration, thus maintaining the skin in its normal state and further preventing rough skin, improving skin roughness, and suppressing the skin inflammation of acne sufferers.

The sunburn preventing cosmetic of the present invention has a superior effectiveness in protecting the skin from hazardous ultraviolet rays. This is believed to be because the zinc oxide covered resin powder adheres uniformly to the surface of the resin powder in a simple dispersed state with the secondary agglomeration of the zinc oxide completely eliminated. Further, at the same time, it has an excellent practical use and cosmetic finish. The inherent characteristics of zinc oxide, i.e., the astringency and inflammation suppression effects, can be simultaneously enjoyed. The deodorant of the present invention has an efficient deodorizing effects with superior safety and practical applicability.

EXAMPLES

The present invention will now be further illustrated by, but is by no means limited to, the following examples, wherein all parts and percentages are expressed on a weight basis unless otherwise noted.

EXAMPLE 1

A 65.0 part amount of spherical Nylon 12 powder (average particle size 6.6 microns) and 35.0 parts of titanium dioxide powder (average particle size 0.2 micron) were mixed together in a Henschel mixer (Mitsui Miike Machinery Co., Ltd., Model FM10B) for 5 minutes, then the obtained mixed powder was mixed and compressed in a tumbling mill (Yamato Scientific Co., universal ball mill) charged with alumina balls (Nippon Kagaku Togyo Co., HD alumina balls, 3 mm ϕ) for 14 hours. Inspection by a scanning type electron microscope (Hitachi Ltd., Model S-510 scanning electron microscope) confirmed that a composite powder with a particle structure shown in FIG. 1 was obtained. This composite powder was spherical in shape, featured Nylon 12 spherical powder substantially completely covered by titanium dioxide powder, displayed a suitable hiding power and hydrophilicity, and had an excellent smoothness. Further, it had a superior stability against separation of the coating powder due to shearing force, etc.

The evaluation of the smoothness was made by measurement of the coefficient of dynamic friction. Note that the powder friction test apparatus (Journal of the Society of Powder Technology, vol. 21, No. 9, p. 565, 1984) was a special order item, and featured an iron plate set horizontally, to which a double sided tape was attached. The sample was set thereon, and a load (5 to

70 g/cm²) was applied to an aluminum attachment. The slipping stress when the attachment was moved right and left at a speed of 10 mm per second was measured by a strain gauge and the coefficient of kinetic friction obtained from the relationship of the load and slipping stress.

The coefficient of dynamic friction of the composite powder obtained was 0.38, a considerably low value compared with the 0.60 of titanium dioxide and about the same level as the 0.39 of Nylon 12 spherical powder, and thus indicated a good smoothness. The hiding power was measured by a cryptometer. The hiding power of the composite powder was high—corresponding to 30 percent of the titanium dioxide powder. Further as a test of the stability against separation of the coating powder, the obtained composite powder was dispersed in liquid paraffin to make a slurry and then subjected to colloid milling. The coating powder did not separate due to the milling, as shown by observation of the particle structure of the tested powder by a scanning type electron microscope (Hitachi Ltd., Model S-510 electron microscope) (FIG. 2).

COMPARATIVE EXAMPLE 1

In the same way as in Example 1, 63.0 parts of Nylon 12 spherical powder (average particle size 6.6 microns) were mixed with 37.0 parts of titanium dioxide powder (average particle size 0.2 micron) in a Henschel mixer (Mitsui Miike Machinery Co., Ltd., FM10B) for 5 minutes. Next, the mixed powder was placed in a tumbling mill (Yamato Scientific Co., universal ball mill) charged with alumina balls (Nihon Kagaku Tokyo Co., HD alumina balls 20 mm ϕ) and mixed and compressed for 14 hours.

The obtained powder, as clear from the results of observation by the scanning type electron microscope (Hitachi Ltd., Model S-510 scanning electron microscope), which are shown in FIG. 3, featured Nylon 12 spherical powder which was not completely covered by the titanium dioxide powder and conspicuous gaps appeared on the surface of the composite powder. Note that even if the composite powder were further mixed for a long time, the covering would remain incomplete and, further, the Nylon 12 spherical powder would be deformed and destroyed. The composite powder shown in FIG. 3 had hiding power and displayed hydrophilicity, but the coefficient of dynamic friction was 0.45 and thus the smoothness was extremely poor. A test was run on the stability against separation of the coating powder in the same way as in Example 1 with colloid milling. Observation of the particle structure by a scanning type electron microscope (Hitachi Ltd., Model S-510 scanning electron microscope) confirmed, as shown in FIG. 4, conspicuous separation of the coating powder.

EXAMPLE 2

A 60.0 part portion of hydrophilic calcium secondary phosphate powder (average particle size 30 microns) was mixed with 40.0 parts of hydrophobic polystyrene powder (average particle size 3 microns) in a Henschel mixer (Mitsui Miike Machinery Co., Ltd., FM10B) for 5 minutes, then the obtained mixed powder was placed in a vibration ball mill (Nihon Spindle Seizo Co., TKM) charged with alumina balls (Nippon Kagaku Togyo Co., HD alumina balls, 5 mm ϕ) and mixed and compressed for 2 hours.

The obtained composite powder featured calcium secondary phosphate powder substantially completely

covered by the polystyrene powder, displayed hydrophobicity, and had an improved smoothness compared with the core powder, calcium secondary phosphate.

EXAMPLE 3

A 65.0 part portion of hydrophobic polystyrene powder (average particle size 15 microns) was mixed with 35.0 parts of hydrophilic spherical silica powder (average particle size 2 microns) in a small sized pulverizer (Kyoritsu Riko Co., SK-M10) for 1 minute, then the obtained mixed powder was placed in a satellite mill (Mitamura Riken Kogyo Co., centrifugal ball mill) charged with alumina balls (Nippon Kagaku Tokyo co., HD alumina balls, 2 mmφ) and mixed and compressed for 1 hour.

The obtained composite powder featured substantially complete coverage and displayed hydrophilicity.

EXAMPLE 4

A 70.0 part amount of cellulose spherical powder (average particle size 3 microns) was mixed and compressed with 30.0 parts of ultramarine blue (average particle size 0.3 micron) in a tumbling mill (Yamato Scientific Co., universal ball mill) charged with alumina balls (Nippon Kagaku Tokyo Co., HD alumina balls, 3 mmφ) for 10 hours.

The obtained composite powder featured substantially complete coverage and had a significantly improved smoothness compared with ultramarine blue.

EXAMPLE 5

A 72.0 part amount of nonmagnetic polystyrene spherical powder (average particle size 8 microns) was placed with 28.0 parts of magnetic iron oxide (average particle size 0.3 micron) in a vibration ball mill (Nihon Spindle Seizo Co., VKM-2) charged with alumina balls (Ashizawa alumina balls, 2 mmφ) and mixed and compressed for 3 hours.

The obtained composite powder featured substantially complete coverage and displayed magnetic properties and hydrophilicity.

EXAMPLE 6

A 61.0 part portion of spherical polystyrene powder (average particle size 100 microns) was placed with 9.0 parts of aluminum powder (average particle size 5 microns) in a satellite mill (Mitamura Riken Kogyo Co., centrifugal ball mill) charged with alumina balls (Ashizawa alumina balls, 1 mmφ) and mixed and compressed for 30 minutes.

The obtained composite powder featured substantially complete coverage and the outer appearance thereof had a metallic luster.

EXAMPLE 7: FACIAL FOUNDATION

(Composition)	
Component	(%)
(1) 40% titanium oxide covered spherical cellulose*	15.0
(2) Silicone treated mica	40.0
(3) Silicone treated talc	20.45
(4) Silicone treated iron oxide	6.5
(5) Titanium oxide	5.0
(6) Trimethylolpropane triisostearate	5.0
(7) Squalane	3.0
(8) Beeswax	2.0
(9) Sorbitan trioleate	1.0
(10) Preservative	0.5

-continued

(Composition)	
Component	(%)
(11) Vitamin E	0.05
(12) Butylmethoxybenzoylmethane	1.0
(13) Perfume	0.5

*In the same way as in Example 1, 40 parts of spherical cellulose powder (average particle size 10 microns) were mixed with 40 parts of titanium dioxide powder (average particle size 0.2 micron) in a Henschel mixer for 5 minutes, then the obtained mixed powder was mixed and compressed in a vibration ball mill charged with alumina balls (Nippon Kagaku Tokyo Co., HD alumina balls, 2 mmφ) for 20 hours.

Production Process

Components (1) to (5) were mixed in a Henschel mixer. To this was added and mixed a mixture of components (6) to (13) heated and melted together. This was then pulverized and shaped into a shallow dish form to give a facial foundation. The foundation had covering power, and at the same time, was easy to apply and gave a beautiful finish.

EXAMPLE 8: OILY FOUNDATION

(Composition)	
Component	(%)
(1) Titanium oxide	6.0
(2) 35% titanium oxide covered spherical nylon powder*	7.0
(3) Kaolinite	12.0
(4) Muscovite	23.7
(5) Red iron oxide	1.0
(6) Yellow iron oxide	0.7
(7) Black iron oxide	0.1
(8) Squalane	27.0
(9) Cetyl 2-ethylhexanoate*	16.0
(10) Sorbitan sesquioleate	1.0
(11) Aristo wax	4.0
(12) Carnauba wax	1.3
(13) Perfume	1.3

*In the same way as in Example 1, 65.0 parts of spherical Nylon 12 powder (average particle size 0.6 microns) were mixed with 35 parts of titanium dioxide powder (average particle size 0.2 micron) in a Henschel mixer for 5 minutes, then the obtained mixed powder was mixed and compressed in a tumbling mill charged with alumina balls (Nippon Kagaku Tokyo Co., HD alumina balls, 3 mmφ) for 14 hours.

Production Process

Components (8) and (9) and component (10) were mixed at 80° C. To this were added components (1), (2), (3), (4), (5) to (6), and (7). These were mixed with a mixer, then subjected to colloid milling. On the other hand, components (11) and (12) were heated to melting point, then added to and mixed with the above-mentioned mixture. The entire mixture was deaerated, then component (13) slowly mixed in. This was then filled into a shallow dish at 80° C. and cooled, thereby giving the oily foundation.

COMPARATIVE EXAMPLES 2 AND 3

In the composition of Example 8, component (2) was replaced by the composite powder of Example 2 (Comparative Example 2) or untreated nylon powder (Comparative Example 3). This was then prepared by the same method as in Example 8.

An organoleptic evaluation was conducted on the products of Example 8 and Comparative Examples 2 and 3, the results being shown in Table 1. As to the method of evaluation, a panel of 10 experts rated the products in five stages, 1 to 5. The following symbols indicate the average values:

- ... 4.5 to 5.0
 ○ ... 3.5 to 4.4

TABLE I

Sample	Appli- cation	Cover- ing power	Clo- se- ness of feel	Streak- ing/ blotch	Finish	General
Ex. 8	○	⊙	○	⊙	⊙	⊙
C. Ex. 2	Δ	○	x	x	x	Δ
C. Ex. 3	○	Δ	x	xx	xx	x

As clear from Table I, the oily foundation of the present invention is superior to those of the conventional comparative examples in all items of the organoleptic evaluation. The same conclusion as in the example can be drawn for oily stick foundations wherein the product is filled into a stick-like container.

EXAMPLE 9: POWDER FOUNDATION

(Composition)	
Component	(%)
(1) 30% titanium oxide covered polyethylene*	16.0
(2) Talc	20.8
(3) Muscovite	50.0
(4) Red iron oxide	0.7
(5) Yellow iron oxide	1.0
(6) Black iron oxide	0.1
(7) Silicone oil	1.0
(8) Cetyl 2-ethylhexanoate	9.0
(9) Sorbitan sesquioleate	1.0
(10) Preservative	0.3
(11) Perfume	0.1

*In the same way as in Example 1, 70.0 parts of spherical polyethylene (average particle size 4 microns) were mixed with 30 parts of titanium dioxide (average particle size 0.3 micron) in a Henschel mixer for 5 minutes, then the obtained mixed powder was mixed and compressed in a tumbling mill charged with alumina balls (Nippon Kagaku Tokyo Co., HD alumina balls 3 mmφ) for 8 hours.

Production Process

Components (1) to (6) were mixed in a Henschel mixer. To this was added and mixed a mixture of components (9) to (11) heated and melted together. This was then pulverized and shaped into a shallow dish form to give a powder foundation. The powder foundation was easy to apply and gave a beautiful finish.

EXAMPLE 10: BRUSHER

(Composition)	
Component	(%)
(1) Talc	15.0
(2) Sericite	65.0
(3) 10% red iron oxide covered spherical cellulose*	4.0
(4) 5% yellow iron oxide covered spherical cellulose**	2.0
(5) 5% ultramarine blue covered spherical cellulose***	2.0
(6) C.I. 15630	0.1
(7) Titanium mica type pearling agent	3.0
(8) Squalane	3.0
(9) 2-Ethylhexyl palmitate	5.0
(10) Preservative	0.3

-continued

(Composition)	
Component	(%)
(11) Perfume	0.1

*In the same way as in Example 1, 90 parts of spherical cellulose (average particle size 20 microns) were mixed with 10 parts of red iron oxide (average particle size 0.1 micron) in a Henschel mixer for 5 minutes, then the obtained mixed powder was mixed and compressed in a tumbling mill charged with alumina balls (Nippon Kagaku Tokyo Co., HD alumina balls, 3 mmφ) for 12 hours.

**In the same way as in Example 1, 95 parts of spherical cellulose (average particle size 20 microns) were mixed with 5 parts of yellow iron oxide (average particle size 0.2 micron) in a Henschel mixer for 5 minutes, then the obtained mixed powder was mixed and compressed in a tumbling mill charged with alumina balls (Nippon Kagaku Tokyo Co., HD alumina balls, 3 mmφ) for 12 hours.

***In the same way as in Example 1, 95 parts of spherical cellulose (average particle size 20 microns) were mixed with 5 parts of ultramarine blue (average particle size 2 microns) in a Henschel mixer for 5 minutes, then the obtained mixed powder was mixed and compressed in a tumbling mill charged with alumina balls (Nippon Kagaku Tokyo Co., HD alumina balls, 3 mmφ) for 12 hours.

Production Process

Components (1) to (6) were mixed in a Henschel mixer. To this was sprayed and mixed a mixture of components (8) to (11) heated and melted together. This was then pulverized, added with component (7) and mixed, then shaped into a shallow dish form to give the brusher.

COMPARATIVE EXAMPLE 4

In the Composition of Example 10, components (3), (4), and (5) were replaced with 0.4 percent red iron oxide, 0.1 percent yellow iron oxide, 0.1 percent ultramarine blue, and 7.4 percent spherical cellulose. Otherwise, the same procedure was followed as in Example 10 to make the brusher.

The brusher of Example 10 featured no uneven color, unlike that of Comparative Example 4.

EXAMPLE 11: Lipstick

(Composition)	
Component	(%)
(1) Hydrocarbon wax	3.0
(2) Candelilla wax	1.0
(3) Glyceryl isostearate	40.0
(4) Liquid paraffin	44.0
(5) Titanium oxide	2.0
(6) 10% C.I. 15585 covered spherical methyl methacrylate resin*	6.8
(7) Organic pigment	3.0
(8) Perfume	0.2

*In the same way as in Example 1, 90 parts of spherical methyl methacrylate resin (average particle size 10 microns) were mixed with 10 parts of Red No. 204 (average particle size 0.2 micron) in a Henschel mixer for 5 minutes, then the obtained mixed powder was mixed and compressed in a tumbling mill charged with alumina balls (Nippon Kagaku Tokyo Co., HD alumina balls, 3 mmφ) for 14 hours.

Production Process

Components (1) to (4) were heated and melted at 85° C. To this was added and stirred components (5) to (7). Next, component (8) was mixed in with stirring. This was filled into a container to make the lipstick. The lipstick featured no color separation and was easy to apply.

EXAMPLE 12: Emulsified Foundation

(Composition)	
Component	(%)
(1) Stearic acid	0.4
(2) Isostearic acid	0.3

-continued

(Composition)	
Component	(%)
(3) Cetyl 2-ethylhexanoate	4.0
(4) Liquid paraffin	11.0
(5) POE (10) stearyl ester	2.0
(6) Talc	15.0
(7) 50% pigment covered spherical polyethylene*	7.0
(8) Cetyl alcohol	0.3
(9) Preservative	0.09
(10) Triethanol amine	0.42
(11) Propylene glycol	5.0
(12) Ion exchange water	54.19
(13) Perfume	0.3

*In the same way as in Example 1, 50 parts of spherical polyethylene powder (average particle size 5 microns) were mixed with 40 parts of titanium dioxide (average particle size 0.2 micron), 3.5 parts of red iron oxide (average particle size 0.1 micron), 5.5 parts of yellow iron oxide (average particle size 0.2 micron), and 1 part of black iron oxide (average particle size 0.2 micron) in a Henschel mixer for 5 minutes, then the obtained mixed powder was mixed and compressed in a tumbling mill charged with alumina balls (Nippon Kagaku Tokyo Co., HD alumina balls, 3 mmφ) for 12 hours.

Production Process

Components (1) to (9) were heated, melted and mixed at 85° C. To this was gradually added a mixture of components (10) to (12) which were heated, melted, and mixed at 85° C., for emulsification. The temperature at the time of emulsification was held for 10 minutes and the mixture stirred. It was then cooled, while stirring, to 45° C. To this was added component (13). The cooling and stirring continued until 35° C., then the product was taken out and filled into a container to make the emulsified foundation. The emulsified foundation featured no uneven color or color separation and was easy to apply.

EXAMPLE 13: Eyeliner

(Composition)	
Component	(%)
(1) Black iron oxide	3.0
(2) 50% ultramarine blue covered spherical alumina*	4.0
(3) Vinyl acetate resin emulsion	45.0
(4) Glycerin	5.0
(5) Polyoxyethylene (20 mol) sorbitan monooleate	1.0
(6) Carboxymethylcellulose (10% aqueous solution)	15.0
(7) Acetyltributyl citrate	1.0
(8) Purified water	19.0
(9) Perfume	Suitable amt
(10) Preservative	Suitable amt

*In the same way as in Example 1, 50 parts of spherical alumina (average particle size 25 microns) were mixed with 50 parts of ultramarine blue (average particle size 2 microns) in a Henschel mixer for 5 minutes, then the obtained mixed powder was mixed and compressed in a vibration ball mill charged with alumina balls (Nippon Kagaku Tokyo Co., HD alumina balls, 4 mmφ) for 24 hours.

Production Process

To component (8) were added components (4) and (5). These were heated to dissolve, then added with components (1) and (2) and subjected to colloid milling (dye portion). The other components were mixed and heated at 70° C. To this was added the above dye portion. This was uniformly dispersed by a homogenizer. As a result, an eyeliner with no color separation and with which lines could be smoothly drawn, was obtained.

EXAMPLE 14: Eyeshadow

(Composition)	
Component	(%)
(1) 25% black iron oxide and 25% prussian blue covered spherical silica*	10.0
(2) 25% red iron oxide and 25% yellow iron oxide covered spherical silica**	3.0
(3) Talc	7.0
(4) Kaolinite	15.0
(5) Nacreous pigment	15.0
(6) Japan wax	20.0
(7) Stearic acid	10.0
(8) Beeswax	5.0
(9) Hardened castor oil	5.0
(10) Vaseline	4.0
(11) Lanolin	3.0
(12) Squalane	3.0
(13) Preservative, antioxidant	Suitable amt

*A 50 part amount of spherical silica (average particle size 10 microns) was mixed with 25 parts of black iron oxide (average particle size 0.2 micron) and 25 parts of prussian blue (average particle size 0.1 micron) in a Henschel mixer for 5 minutes, then the obtained mixed powder was mixed and compressed in a tumbling mill charged with alumina balls (Nippon Kagaku Tokyo Co., HD alumina balls, 3 mmφ) for 24 hours.

**In the same way as in Example 1, 50 parts of spherical silica (average particle size 10 microns) were mixed with 25 parts of red iron oxide (average particle size 0.1 micron) and 25 parts of yellow iron oxide (average particle size 0.2 micron) in a Henschel mixer for 5 minutes, then the obtained mixed powder was mixed and compressed in a tumbling mill charged with alumina balls (Nippon Kagaku Tokyo Co., HD alumina balls, 3 mmφ) for 24 hours.

Production Process

Components (1) to (5) were mixed well with a blender (powder portion). The other components were mixed, heated and melted, then the above powder portion added thereto and the mixture kneaded well and shaped into a core. This was placed between wood to make a pencil form. An eyeshadow was obtained which had no uneven color and an easy applicability.

EXAMPLE 15: Solid Powder Form Skin Treatment Agent

(Composition)	
Component	(%)
(1) Talc	49.8
(2) Magnesium stearate	5.0
(3) Hydroxyapatite powder (10%) covered spherical nylon*	45.0
(4) Perfume	0.1
(5) Bactericide	0.1

*In the same way as in Example 1, 90 parts of spherical nylon powder (average particle size 5 microns) were mixed with 10 parts of hydroxyapatite powder (average particle size 0.1 micron) in a Henschel mixer for 5 minutes, then the obtained mixed powder was mixed and compressed in a vibration ball mill charged with alumina balls (2 mmφ) for 6 hours.

Production Process

Components (1) to (3) and (5) were mixed well with a blender while component (4) was sprayed thereon. The mixture was shaped into a shallow dish to give a solid powder form skin treatment agent.

COMPARATIVE EXAMPLE 5

(Composition)

(Composition)	
Component	(%)
(1) Talc	49.8

-continued

(Composition)	
Component	(%)
(2) Magnesium stearate	5.0
(3) Hydroxyapatite powder	4.5
(4) Spherical nylon	40.5
(5) Perfume	0.1
(6) Bactericide	0.1

CONFIRMATION OF EFFECTS BY TEST USE

Twenty test subjects suffering from rough skin used the powder skin treatment agent obtained in Example 15 and the agent of Comparative Example 5, in which the hydroxyapatite was not combined to make a composite powder but merely added therein, on their faces for a period of three months and the effects on the prevention of rough skin observed. The results are shown in Table 2. Compared with Comparative Example 2, with the agent of Example 15, a large number of the test subjects, 30 percent, stated that there had been a clear improvement in their rough skin or some improvement in their rough skin, thus indicating that the composite powder of hydroxyapatite was more effective against rough skin.

TABLE 2

	Ex. 15	C. Ex. 5
Clear improvement in rough skin	8 subj.	3 subj.
Some improvement in rough skin	10	9
No effect on rough skin	2	8

EXAMPLE 16 Powder Form Skin Treatment

(Composition)

(Composition)	
Component	(%)
(1) Talc	49.5
(2) Hydroxyapatite powder (25%) covered spherical polyethylene*	50.0
(3) Perfume	0.05

*A 75 parts amount of spherical polyethylene powder (average particle size 10 microns) was mixed with 25 parts of hydroxyapatite powder (average particle size 0.2 micron) in a Henschel mixer for 5 minutes, then the obtained mixed powder was mixed and compressed in a tumbling mill charged with alumina balls (3 mm) for 6 hours.

Production Process

Components (1) to (2) were mixed well with a blender while component (3) was sprayed uniformly thereon, thus giving a powder skin treatment agent.

COMPARATIVE EXAMPLE 6

(Composition)	
Component	(%)
(1) Talc	49.95
(2) Hydroxyapatite powder	12.5
(3) Spherical polyethylene powder	37.5
(4) Perfume	0.05
(Production Process)	
Same as Example 16.	

CONFIRMATION OF EFFECTS BY TEST USE

Ten test subjects suffering from acne used the powder skin treatment agent obtained in Example 16 and the

agent of Comparative Example 6, in which the hydroxyapatite was not combined to make a composite powder but merely added therein, on their faces for a period of three months and the effects on the prevention of acne observed. The results are shown in Table 3. Compared with Comparative Example 6, with the agent of Example 16, a large number of the test subjects, 40 percent, stated that there had been a clear improvement in the inflammation or some improvement in the inflammation, thus indicating that the composite powder alleviated inflammation induced by acne.

TABLE 3

	Ex. 16	C. Ex. 6
Clear improvement in inflammation	6 subj.	3 subj.
Some improvement in inflammation	3	2
No effect	1	5

EXAMPLE 17: OINTMENT

(Composition)	
Component	(%)
(1) Ceresine	20.0
(2) Liquid paraffin	18.0
(3) POE (10 mol) monooleate ester*	0.25
(4) Glyceryl monostearate	0.25
(5) Vaseline	35.0
(6) Hydroxyapatite powder (10%) covered spherical nylon*	5.0
(7) Purified water	17.5
(8) Propylene glycol	4.0

*See asterisked note of Example 15.

Production Process

Components (1) to (5) were mixed and melted at 70° C. (oil phase) and component (6) added thereto. Component (8) was melted into component (7) and the two held at 70° C. These were added to the oil phase. The mixture was emulsified uniformly with a homogenizing mixer, then cooled to give the ointment.

The ointment obtained in Example 17 featured superior effectiveness in the prevention of rough skin in actual use compared with an ointment wherein the hydroxyapatite was not combined to make a composite powder but merely added therein.

EXAMPLE 18: POWDER FOUNDATION

(Composition)	
Component	(%)
(1) Sericite	54.28
(2) Talc	20.0
(3) Hydroxyapatite powder (33%) covered cellulose*	3.0
(4) Titanium dioxide	6.5
(5) Iron oxide	3.5
(6) Trimethylolpropane triisostearate	5.0
(7) Squalane	6.0
(8) Sorbitan sesquioleate	1.0
(9) Preservative	0.5
(10) Antioxidant	0.02
(11) Perfume	0.2

*A 67 parts amount of spherical cellulose powder (average particle size 25 microns) was mixed with 3 parts of hydroxyapatite powder (average particle size 1.2 micron) and processed by the same method as in the asterisked note of Example 16.

PRODUCTION PROCESS

Components (1) to (5) were mixed with a Henschel mixer. To this was added a mixture of components (6) to (11) which had been heated and melted together. This was mixed and pulverized, and then shaped into a shallow dish to give the powder foundation.

EXAMPLE 19: SOLID WHITE POWDER

(Composition)	
Component	(%)
(1) Talc	87.9
(2) Hydroxyapatite powder (7%) covered spherical silica*	10.0
(3) Liquid paraffin	2.0
(4) Perfume	0.1

*A 93 part amount of spherical silica powder (average particle size 1 micron) was mixed with 7 parts of hydroxyapatite powder (average particle size 0.05 micron) and processed by the same method as in the asterisked note of Example 15.

Production Process

Components (1) and (2) were mixed well with a blender while component (3) was uniformly sprayed thereon. This was shaped into a shallow dish to give a solid white powder.

EXAMPLE 20: Baby Powder

(Composition)	
Component	(%)
(1) Talc	80.0
(2) Calcium carbonate	17.0
(3) Starch	0.5
(4) Hydroxyapatite powder (12%) covered spherical titanium dioxide*	2.0
(5) Bactericide	0.3
(6) Preservative	0.2

*An 88 part amount of spherical titanium dioxide powder (average particle size 1 micron) was mixed with 12 parts of hydroxyapatite powder (average particle size 0.1 micron) and processed by the same method as in the asterisked note of Example 15.

Production Process

Components (1) to (6) were mixed well with a blender to give the baby powder.

EXAMPLE 21: Pack

(Composition)	
Component	(%)
(1) Polyvinyl alcohol	15.0
(2) Polyethylene glycol	3.0
(3) Propylene glycol	7.0
(4) Ethanol	10.0
(5) Hydroxyapatite powder (7%) covered spherical silica*	10.0
(6) Methylparaben	0.05
(7) Perfume	0.15
(8) Purified water	54.8

*See asterisked note of Example 19.

Production Process

Components (2), (3), and (6) were added to component (8) and dissolved therein. Next, component (1) was added, then the mixture heated and stirred for dissolution, then component (5) dispersed therein. Then this was added components (4) and (7); the mixture was stirred for dissolution, and a pack was formed.

EXAMPLE 22: Cream

(Composition)	
Component	(%)
(1) Cetostearyl alcohol	3.5
(2) Squalane	20.0
(3) Beeswax	3.0
(4) Lanolin	5.0
(5) Ethylparaben	0.3
(6) POE (20 mol) sorbitan monooleate ester*	2.0
(7) Glyceryl monostearate	2.0
(8) Hydroxyapatite powder (33%) covered spherical cellulose*	5.0
(9) Perfume	0.1
(10) 1,3-butylene glycol	5.0
(11) Glycerine	5.0
(12) Purified water	49.1

*See asterisked note of Example 18.

Production Process

Components (1) to (6) and (9) were heated to melting point and maintained at 75° C. (oil phase). Components (10) and (11) were dissolved in component (12), then component (8) added and dispersed therein and the mixture heated to 75° C. (water phase). The oil phase was added to the water phase, then the two were emulsified by a homogenizer and cooled to form the cream.

The cosmetics obtained in Examples 18 to 22, compared with cosmetic wherein, instead of adding the hydroxyapatite composite powders of the examples, use was made of another, noncomposite powder, feature a good feel during application in actual use and a uniform spreadability, and further, help maintain skin smoothness and are effective against skin roughness.

EXAMPLE 23: SUNBURN PREVENTING FACIAL FOUNDATION

(Composition)	
Component	(%)
(1) 15% zinc oxide covered nylon powder*	20.0
(2) Silicone treated mica	40.0
(3) Silicone treated talc	20.45
(4) Silicone treated iron oxide	7.5
(5) Trimethylolpropane triisostearate	5.0
(6) Squalane	3.0
(7) Beeswax	2.0
(8) Sorbitan trioleate	1.0
(9) Propylparaben	0.5
(10) Vitamin E	0.05
(11) Perfume	0.5

*Here, 150 g of zinc oxide (average particle size 0.05 microns) and 850 g of spherical nylon powder (average particle size 3 microns) were charged into a 5 liter capacity tumbling mill and treated for 3 hours. The obtained powder was observed by electron microscope, whereby it was found that the nylon powder was completely covered by the 15% zinc oxide.

Production Process

Components (1) to (4) were mixed in a Henschel mixer. To this was added and mixed a mixture of components (5) to (11) heated and melted together. This was then pulverized and shaped into a shallow dish form to give a sunburn preventing facial foundation.

The foundation of Example 23 was easy to apply and gave a natural finish.

COMPARATIVE EXAMPLE 7: SUNBURN PREVENTION FACIAL FOUNDATION

In the composition of Example 23, component (1) was omitted and 3 percent zinc oxide and 17 percent nylon powder were compounded without covering treatment. Otherwise, the sunburn preventing facial foundation was obtained in the same way as in Example 23.

The foundation of Comparative Example 6 was difficult to apply and did not give a satisfactory feeling during use.

EXAMPLE 24: SUNBURN PREVENTING CREAM

Example 24: Sunburn Preventing Cream (Composition)	
Component	(%)
(1) 40% zinc oxide covered polyethylene*	5.0
(2) Cetanol	5.0
(3) Stearic acid	3.0
(4) Vaseline	5.0
(5) Squalane	2.0
(6) Isopropylmyristate	2.0
(7) Liquid paraffin	5.0
(8) Glyceryl monoisostearate	3.0
(9) Ethylparaben	0.2
(10) Perfume	0.2
(11) Glycerine	10.0
(12) Propylene glycol	5.0
(13) Hyaluronic acid	0.01
(14) Potassium hydroxide	0.2
(15) Purified water	54.39

*Here, 400 g of zinc oxide (average particle size 0.1 micron) and 600 g of polyethylene powder (average particle size 10 microns) were charged into a 5 liter capacity vibration ball mill and treated for 1 hour.

The obtained powder was observed by an electron microscope, whereby it was found that the polyethylene powder was completely covered by the 40 percent zinc oxide.

Production Process

Components (1) to (10) were heated and stirred to form the oil phase. Components (11) to (15) were mixed and heated to 70° C. to ensure complete dissolution to form the water phase. The oil phase was mixed in the water phase and an emulsion formed by an emulsifier. The emulsion was cooled by a heat exchanger to 30° C., then filled in a container to give the sunburn preventing cream.

COMPARATIVE EXAMPLE 8: SUNBURN PREVENTING CREAM

In the composition of Example 24, component (1) was omitted and 2 percent zinc oxide and 3 percent polyethylene powder were compounded without covering treatment. Otherwise, the sunburn preventing cream was obtained in the same way as in Example 24.

EXAMPLE 25: SUNBURN PREVENTING LOTION

Example 25: Sunburn Preventing Lotion (Composition)	
Component	(%)
(1) 30% zinc oxide covered polymethyl metacrylate resin	7.0
(2) Stearic acid	1.0
(3) Dimethylpolysiloxane (5CS/25° C.)	10.0
(4) Glycerylmonoisostearate	1.5
(5) Ethylparaben	0.2

-continued

Example 25: Sunburn Preventing Lotion (Composition)	
Component	(%)
(6) Butylparaben	0.2
(7) Perfume	0.15
(8) Glycerine	5.0
(9) Montmorillonite	0.5
(10) Potassium hydroxide	0.2
(11) Purified water	74.25

Production Process

Components (1) to (7) were heated and stirred to form the oil phase. Components (8) to (11) were mixed and heated to 70° C. to ensure complete dissolution to form the water phase. The oil phase was mixed in the water phase and an emulsion formed by an emulsifier. The emulsion was cooled by a heat exchanger to 30° C., then filled in a container to give the sunburn preventing lotion.

COMPARATIVE EXAMPLE 9: SUNBURN PREVENTION LOTION

In the composition of Example 25, component (1) was omitted and 2.1 percent zinc oxide and 4.9 percent polymethyl metacrylate were compounded without covering treatment. Otherwise, the sunburn preventing lotion was obtained in the same way as in Example 25.

EXAMPLE 26: SUNBURN PREVENTING POWDER FOUNDATION

Example 26: Sunburn Preventing Powder Foundation (Composition)	
Component	(%)
(1) 10% zinc oxide covered nylon powder	16.0
(2) Talc	20.8
(3) Muscovite	50.0
(4) Red iron oxide	1.0
(5) Yellow iron oxide	0.7
(6) Black iron oxide	0.1
(7) Dimethylpolysiloxane (5CS/25° C.)	1.0
(8) Cetyl 2-ethylhexanoate	9.0
(9) Sorbitan sesquioleate	1.0
(10) Propylparaben	0.3
(11) Perfume	0.1

Production Process

Components (1) to (6) were mixed in a Henschel mixer. To this was added and mixed a mixture of components (7) to (11) heated and melted together. This was then pulverized and shaped into a shallow dish form to give a sunburn preventing powder foundation.

COMPARATIVE EXAMPLE 10: SUNBURN PREVENTING POWDER FOUNDATION

In the composition of Example 26, component (1) was omitted and 1.6 percent zinc oxide and 14.4 percent nylon powder were compounded without covering treatment. Otherwise, the sunburn preventing powder foundation was obtained in the same way as in Example 26.

The products of Examples 23 to 26 and Comparative Examples 6 to 9, obtained as explained above, were measured for effectiveness in blocking ultraviolet rays.

The effectiveness in blocking ultraviolet rays was determined using the ultraviolet sensitive composition shown below:

Formulation of Ultraviolet Sensitive Composition (Japanese Patent Application No. 60-250678)	
Solution I	
Leukocrystal violet	1.0 g
Tetrabromodimethylsulfone	0.1 g
Ethylene-vinyl acetate copolymer	10 g
Toluene	100 ml
Solution II	
N,N-dimethylparaaminobenzoate	7 g
2-ethylhexylester	10 g
Ethylene-vinyl acetate copolymer	10 g
Toluene	100 ml

Solutions I and II were separately prepared. First, solution I was applied on photographic paper in a thickness of 1 g/m² solids content, then solution II was applied on the top for a thickness of 5 g/m² solids content.

The ultraviolet sensitive composition was irradiated by ultraviolet light. In accordance with the increase in the amount of ultraviolet light irradiated, the paper changed color from white to light purple, to purple, and to dark purple. A 40 mg amount of the sample to be measured was mixed in 12 g of castor oil, then a roller treatment applied for an even dispersion. Transparent PET film was placed on the above-mentioned ultraviolet sensitive composition, formed in a cylindrical shape with a diameter of 5 cm. To this, 1.5 g of the sample was applied in an even thickness. An ultraviolet lamp was turned on for 8 minutes. The PET film was removed with each sample and the color-forming ultraviolet sensitive composition was measured using a Hitachi 607 spectrophotometer to calculate the color difference with an LAB coordinate system, based on the color of the ultraviolet sensitive composition under zero ultraviolet irradiation.

The results are shown in Table 4.

TABLE 4

	Color difference
Example 23	28
Comparative Example 6	39
Example 24	36
Comparative Example 7	45
Example 25	41
Comparative Example 8	57
Example 26	29
Comparative Example 9	39

As understood from Table 4, the color differences of the examples were smaller than those of the corresponding comparative examples, indicating a higher effectiveness in blocking ultraviolet rays. That is, by depositing zinc oxide uniformly on the surface of a resin powder, it is possible to raise the effectiveness in scattering ultraviolet rays.

EXAMPLE 27: SUNBURN PREVENTING LOOSE POWDER

Example 27: Sunburn Preventing Loose Powder (Composition)	
Component	(%)
(1) 60% zinc oxide covered polystyrene powder	55.0
(2) Talc	10.0
(3) Mica	29.5
(4) Red iron oxide	2.0
(5) Yellow iron oxide	2.0
(6) Black iron oxide	1.0
(7) Perfume	0.5

Components (1) to (7) were mixed in a Henschel mixer to obtain the sunburn preventing loose powder.

The product of Example 27 had a smooth feeling during use and was highly effective in blocking out ultraviolet light.

EXAMPLE 28: SUNBURN PREVENTING STICK COSMETIC

Example 28: Sunburn Preventing Stick Cosmetic (Composition)

Component	(%)
(1) 5% zinc oxide/3% silicic acid anhydride covered teflon powder	10.0
(2) Titanium oxide	10.0
(3) Mica	16.0
(4) Red iron oxide	1.5
(5) Yellow iron oxide	1.5
(6) Black iron oxide	1.0
(7) Squalane	39.4
(8) Trimethylolpropane tri-2-ethylhexanoate	10.0
(9) Solid paraffin	6.0
(10) Microcrystalline wax	2.0
(11) Ceresine	1.0
(12) Perfume	0.5
(13) Antioxidant	0.1
(14) Sorbitan sesquiolate	1.0

Production Process

Components (1) to (6) were mixed together, and then added to components (7), (8), (13), and (14), which were heated and stirred, then the mixture further mixed and pulverized. Next, a molten mixture of components (9), (10), (11), and (12) was added to the above mixture. This was fully mixed, then shaped into a stick form to give the sunburn preventing stick cosmetic.

The product of Example 28 had a good ultraviolet blocking effect and had a superior cosmetic effect due to the skin oil fixing action of the zinc oxide and the sweat absorption action of the anhydrous silicic acid.

EXAMPLE 29: DEODORANT POWDER

Composition

A 40 g amount of hydroxyapatite powder (specific surface area 70.4 m²/g, Sumitomo Chemical) and 50 g of nylon (Nylon 12 spherical, average particle size 5 microns, Nylon SP-500, Nikko Rikagaku Sangyo) were mixed using a Mitsui Mike Machinery Co., Model FMI-B Henschel mixer for 10 minutes to homogenize them and obtain the composite powder. Next, the composite powder was used to form a deodorant powder having the following composition.

Component	(%)
Composite powder	40.0
Talc	60.0

Using the above powder, a deodorizing test was conducted by the following method, whereupon it was found that, after the start of the test, in the case of all subjects on the test panel, the underarm odor intensity of the test portion was 5 percent in terms of risk compared with the control portion; which was significantly lower.

Deodorizing Test Method

A panel of six healthy men believing themselves to suffer from underarm odor was used for testing the deodorant containing the composite powder of the present invention. The test product was applied directly to the test underarm a total of four times: once in the morning and once in the afternoon for two days. The untested underarm was used as the control portion.

The judgment was made using the following five stages:

- 0: No underarm odor
- 1: Some underarm odor
- 2: Clear underarm odor
- 3: Strong underarm odor
- 4: Very strong underarm odor

EXAMPLE 30: AEROSOL DEODORANT SPRAY

A 70 ml amount of sintered alumina balls of an average size of 2 mmφ, 20 g of hydroxyapatite (specific surface area 70.4 m²/g), and 80 g of nylon (average particle size 5 microns) were filled into a centrifugal tumbling mill and subjected to ball milling for 30 minutes.

Using the resultant composite powder, an aerosol deodorant spray having the following composition was prepared.

Component	(%)
Freon 11	76.8
Freon 12	19.2
Composite powder	1.5
Talc	1.5
Isopropyl myristate	0.5
Diglyceryl tetra-2-ethylhexanoate	0.5

In actual test use of this spray, even after the start of the test, as shown in FIG. 5, the intensity of underarm odor of the test portions of all test subjects on the panel was 5 percent in terms of risk; significantly lower than the control portions.

FIGS. 6 and 7 show the changes over time of the underarm odor intensity in the case of the aerosol deodorant spray of Example 30 in which the composite powder was replaced with nylon and hydroxyapatite powder. The change over time of the underarm odor intensity in the case of the aerosol deodorant spray of Example 30, on the other hand, is shown in FIG. 5.

EXAMPLE 31: AEROSOL DEODORANT SPRAY

In the same way as in Example 30, 40 g of hydroxyapatite and 60 g of nylon were ball milled. Using the obtained composite powder, an aerosol deodorant spray having the following composition was prepared.

Component	(%)
Freon 11	76.8
Freon 12	19.2
Composite powder	1.0
Talc	2.0
Isopropyl myristate	0.5
Diglyceryl tetra-2-ethylhexanoate	0.5

At the start of the actual test use of this spray, after the start of the test, the intensity of underarm odor of the test portions of all test subjects on the panel was 5

percent in terms of risk; significantly lower than the control portions.

EXAMPLE 32: DEODORANT POWDER

In the same way as in Example 30, 30 g of hydroxyapatite and 70 g of nylon were ball milled. Using the obtained composite powder, a deodorant powder having the following composition was prepared.

Component	(%)
Composite powder	50.0
Talc	50.0

Upon actual test use of the deodorant powder, it was found that, after the start of the test, the intensity of underarm odor of the test portions of all test subjects on the panel was 5 percent in terms of risk; significantly lower than the control portions.

EXAMPLE 33: DEODORANT POWDER

In the same way as in Example 30, 20 g of hydroxyapatite and 80 g of nylon were ball milled. Using the obtained composite powder, a deodorant powder having the following composition was prepared.

Component	(%)
Composite powder	30.0
Talc	70.0

Along with use of the deodorant powder, the intensity of underarm odor of all test subjects on the panel decreased with time, proving the effectiveness of the powder.

EXAMPLE 34: DEODORANT POWDER

Composition

A 50 g amount of zinc oxide (#1 special grade, average particle size 0.5 microns, Sakai Kagaku) and 50 g of nylon (Nylon 12 spherical, average particle size 5 microns, Nylon SP-500, Nikko Rikagaku Sangyo) were mixed using a Mitsui Miike Machinery Co., Model FMI-B Henschel mixer for 10 minutes to homogenize them and obtain the composite powder. Next, the composite powder was used to form a deodorant powder having the following composition.

Component	(%)
Composite powder	50.0
Talc	50.0

Using the above powder, a deodorizing test was conducted by the same method as in Example 29, whereupon it was found that, after the start of the test, in the case of all subjects on the test panel, the underarm odor intensity of the test portion was 5 percent in terms of risk compared with the control portion; which was significantly lower.

EXAMPLE 35: AEROSOL DEODORANT SPRAY

A 70 ml amount of sintered alumina balls of an average size of 2 mmφ, 20 g of zinc oxide (average particle size 20 microns), and 80 g of nylon (average particle size 5 microns) were filled into a centrifugal tumbling mill and subjected to ball milling for 30 minutes.

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Using the resultant composite powder, an aerosol deodorant spray having the following composition was prepared.

Component	(%)
Freon 11	76.8
Freon 12	19.2
Composite powder	1.5
Talc	1.5
Isopropyl myristate	0.5
Diglyceryl tetra-2-ethylhexanoate	0.5

In actual test use of this spray as in Example 29, even after the start of the test, the intensity of underarm odor of the test portions of all test subjects on the panel was 5 percent in terms of risk; significantly lower than the control portions.

EXAMPLE 36: AEROSOL DEODORANT SPRAY

In the same way as in Example 35, 40 g of zinc oxide and 60 g of nylon were ball milled. Using the obtained composite powder, an aerosol deodorant spray having the following composition was prepared.

Component	(%)
Freon 11	76.8
Freon 12	19.2
Composite powder	0.6
Talc	2.4
Isopropyl myristate	0.5
Diglyceryl tetra-2-ethylhexanoate	0.5

At the start of actual test use of this spray, after the start of the test, the intensity of underarm odor of the test portions of all test subjects on the panel was 5 percent in terms of risk; significantly lower than the control portions.

EXAMPLE 37: DEODORANT POWDER

In the same way as in Example 35, 30 g of zinc oxide and 70 g of nylon were ball milled. Using the obtained composite powder, a deodorant powder having the following composition was prepared.

Component	(%)
Composite powder	50.0
Talc	50.0

Upon actual test use of the deodorant powder, it was found that, after the start of the test, the intensity of underarm odor of the test portions of all test subjects on the panel was 5 percent in terms of risk; significantly lower than the control portions.

EXAMPLE 38: DEODORANT POWDER

In the same way as in Example 35, 20 g of zinc oxide and 80 g of nylon were ball milled. Using the obtained composite powder, a deodorant powder having the following composition was prepared.

Component	(%)
Composite powder	30.0
Talc	70.0

32

Along with use of the deodorant powder, the intensity of underarm odor of all test subjects on the panel decreased along with time, proving the effectiveness.

EXAMPLE 39: DEODORANT POWDER

Composition

A 50 g amount of aluminum hydroxychloride and 50 g of nylon (Nylon 12 spherical, average particle size 5 microns, Nylon SP-500, Nikko Rikagaku Sangyo) were mixed using a Mitsui Miike Machinery Co., Model FMI-B Henschel mixer for 10 minutes to homogenize them and obtain the composite powder. Next, the composite powder was used to form a deodorant powder having the following composition.

Component	(%)
Composite powder	0.1
Talc	79.9
Kaolin	20.0

Using the above powder, a deodorizing test was conducted by the same method as in Example 29, whereupon it was found that, after the start of the test, in the case of all subjects on the test panel, the underarm odor intensity of the test portion was 5 percent in terms of risk compared with the control portion; which was significantly lower.

EXAMPLE 40: DEODORANT POWDER

Composition

A 50 g amount of benzalkonium chloride and 50 g of polyethylene (average particle size 5 microns) were mixed using a Mitsui Miike Machinery Co., Model FMI-B Henschel mixer for 10 minutes to homogenize them and obtain the composite powder. Next, the composite powder was used to form a deodorant powder having the following composition.

Component	(%)
Composite powder	5.0
Talc	85.0
Kaolin	10.0

Using the above powder, a deodorizing test was conducted by the same method as in Example 29, whereupon it was found that, after the start of the test, in the case of all subjects on the test panel, the underarm odor intensity of the test portion was 5 percent in terms of risk compared with the control portion; which was significantly lower.

EXAMPLE 41: AEROSOL DEODORANT SPRAY

Using the same composite powder as in Example 39, an aerosol deodorant spray having the following composition was prepared.

Component	(%)
Freon 11	76.8
Freon 12	19.2
Composite powder	0.6
Talc	2.4
Isopropyl myristate	0.5
Diglyceryl tetra-2-ethylhexanoate	0.5

In actual test use of this spray, even after the start of the test, the intensity of underarm odor of the test portions of all test subjects on the panel was 5 percent in terms of risk; significantly lower than the control portions.

EXAMPLE 42: DEODORANT LOTION

A deodorant lotion having the following composition was prepared.

Component	(%)
Purified water	82.0
Ethanol	15.0
Sorbitol	2.0
Composite powder (the same as in Example 39)	1.0

In actual use test of this lotion, even after the start of the test, the intensity of underarm odor of the test portions of all test subjects on the panel was 5 percent in terms of risk; significantly lower than the control portions.

We claim:

1. A composite powder comprising a core powder having an average particle size of 0.5 to 100 μm substantially completely covered with a coating powder having an average particle size of one-fifth or less of the average particle size of the above-mentioned core powder, said core powder being at least one powder selected from the group consisting of polyamide resin, polyethylene resin, acrylic resin, polyester resin, fluorine resin and cellulose resin, and said coating powder being at least one coating powder selected from the group consisting of titanium dioxide, talc, kaolinite, zinc white, magnesium oxide, calcium oxide, barium sulfate, magnesium carbonate, calcium carbonate, silica, calcium secondary phosphate, iron oxide, chromium oxide, chromium hydroxide, ultramarine blue, prussian blue, hydroxyapatite, and silicon treated, activant treated and wax treated powder thereof, aluminum gold, silver, and iron powder and the halogen compounds thereof, said composite powder being produced by dry mixing and dry compressing the organic or inorganic powder constituting the core powder and one or more types of the organic, inorganic, or metallic powders constituting the coating powder, a mixer charged with a ball shaped mixing medium having an average diameter of at most 5 mm being used to produce the composite powder.

2. A skin treatment agent comprising a spherical composite powder produced by dry mixing and dry compressing an organic or inorganic spherical core powder and hydroxyapatite coating powder, so that the spherical core powder having an average particle size of 0.5 to 100 microns is substantially completely covered by the coating powder having an average particle size of one-fifth or less of the average particle size of the above core powder, a mixer charged with a ball shaped mixing

medium having an average diameter of at most 5 mm being used to produce the composite powder, said core powder being at least one powder selected from the group consisting of polyamide resin, polyethylene resin, acrylic resin, polyester resin, fluorine resin and cellulose resin, and said coating powder at least one coating powder selected from the group consisting of titanium dioxide, talc, kaolinite, zinc white, magnesium oxide, calcium oxide, barium sulfate, magnesium carbonate, calcium carbonate, silica, calcium secondary phosphate, iron oxide, chromium oxide, chromium hydroxide, ultramarine blue, prussian blue, hydroxyapatite, and silicon treated, activant treated and wax treated powder thereof, aluminum gold, silver, and iron powder and the halogen compounds thereof.

3. A makeup type cosmetic comprising a spherical composite powder produced by dry mixing and dry compressing a spherical core powder and a coating powder so as to substantially completely cover the spherical core powder having an average particle size of 0.5 to 100 μm with the coating powder having an average particle size of one-fifth or less of the average particle size of the above-mentioned core powder, a mixer charged with a ball shaped mixing medium having an average diameter of at most 5 mm being used to produce the composite powder, said core powder being at least one powder selected from the group consisting of polyamide resin, polyethylene resin, acrylic resin, polyester resin, fluorine resin and cellulose resin, and said coating powder at least one coating powder selected from the group consisting of titanium dioxide, talc, kaolinite, zinc white, magnesium oxide, calcium oxide, barium sulfate, magnesium carbonate, calcium carbonate, silica, calcium secondary phosphate, iron oxide, chromium oxide, chromium hydroxide, ultramarine blue, prussian blue, hydroxyapatite, and silicon treated, activant treated and wax treated powder thereof, aluminum gold, silver, and iron powder and the halogen compounds thereof.

4. A composite powder wherein a polyethylene core powder having an average particle size of 0.5 to 100 μm is substantially completely covered with a coating powder composed of silica having an average particle size of one-fifth or less of the average particle size of the above-mentioned core powder, said composite powder being produced by dry mixing and dry compressing said composite.

5. A process for the production of a composite powder comprising dry mixing and dry compressing a polyethylene core powder and silica, wherein a mixer charged with a ball shaped mixing medium having an average diameter of 0.5 μm or less is used to produce a composite in which said core powder having an average particle size of 0.5 to 100 μm is substantially completely covered by said silica having an average particle size of one-fifth or less of said polyethylene core powder.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,122,418

DATED : June 16, 1992

INVENTOR(S) : Nakane et al.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Col. 33, lines 48-49 Delete " 5m " and substitute -- 5mm --

Col. 34, line 16 Delete " type "

Col. 34, line 52 Delete " 0.5 " and substitute -- 5 --

Signed and Sealed this

Twenty-second Day of March, 1994

Attest:



BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks

United States Patent [19]

Watanabe et al.

[11] Patent Number: 4,603,047

[45] Date of Patent: Jul. 29, 1986

[54] FLAKY PIGMENTS, PROCESS FOR THEIR PREPARATION

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[21] Appl. No.: 663,733

[22] Filed: Oct. 22, 1984

[30] Foreign Application Priority Data

Oct. 21, 1983 [JP] Japan 58-196114
Oct. 21, 1983 [JP] Japan 58-196115

[51] Int. Cl.⁴ A61K 7/021

[52] U.S. Cl. 424/63; 106/291;
106/308 B; 424/69

[58] Field of Search 106/291, 288, 308 B;
424/63, 69

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Primary Examiner—Theodore Morris

Attorney, Agent, or Firm—Millen & White

[57] ABSTRACT

Flaky pigments, in which a flaky substrate, such as in particular, mica, talc or kaolin, are provided with a firmly adhering coating of barium sulphate, if appropriate together with a metal oxide, hydrated metal oxide or metal carbonate, are advantageously used in cosmetics.

16 Claims, No Drawings

FLAKY PIGMENTS, PROCESS FOR THEIR PREPARATION

BACKGROUND OF THE INVENTION

This invention relates to flaky pigments which can be used in cosmetics.

It is known to use flaky powders, such as, for example, mica, e.g., muscovite or sericite, or clay materials, such as kaolin or talc, as the starting material for the preparation of facial powders useful in cosmetics. Since these pigments by themselves do not possess the necessary adhesion and extension properties when used on the skin, when used for the preparation of face powders they are conventionally also mixed with titanium dioxide, metal soaps and calcium carbonate.

SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to markedly improve the properties of the hitherto customary pigments with respect to adhesion capacity and extension on the skin and also with respect to gloss and transparency, e.g., by coating of the flaky substrates.

Upon further study of the specification and appended claims, further objects and advantages of this invention will become apparent to those skilled in the art.

These objects have been achieved and this invention therefore relates to flaky pigments which are characterized in that a flaky substrate is provided with a firmly adhering coating of barium sulphate; if appropriate together with a metal oxide, hydrated metal oxide or metal carbonate.

The invention also relates to a process for the preparation of a flaky pigment, which is characterized in that an aqueous suspension of a flaky substrate is treated, simultaneously or successively, with an aqueous solution containing barium ions and with an aqueous solution containing sulphate ions, and the pigments coated with barium sulphate and then separated off, dried and, if appropriate, calcined.

Moreover, the invention relates to the use of these pigments for the preparation of cosmetic agents.

DETAILED DISCUSSION

The starting material used for the preparation of the pigments according to the invention can be mica, such as, for example, muscovite or sericite, talc, kaolin, etc. For coating, this substrate in a particle size of about 1-100 μm , preferably 1-50 μm , can be suspended in water and, in the simplest case, coated with a layer of barium sulphate. To do this, an aqueous solution containing barium ions as well as an aqueous solution containing sulphate ions are added, either simultaneously or successively, to the aqueous suspension at a temperature of about 5°-100° C., preferably 20°-80° C. Advantageously, the suspension is vigorously stirred during the addition and the solutions are added at such a rate that the precipitated barium sulphate is deposited on the surface of the flaky substrate.

For preparing the solution containing barium ions, all water-soluble barium salts, such as, for example, barium chloride, barium hydroxide, barium nitrate and barium sulphide, are suitable in principle. Because of its advantageous price, ready availability and high purity, barium chloride is preferred. For preparing the solution containing sulphate ions, all soluble sulphates, such as, for example, sodium sulphate, potassium sulphate, magne-

sium sulphate, sodium bisulphate or potassium bisulphate, as well as sulphuric acid can be used.

The quantities in which the reactants are employed are not in themselves particularly critical. In particular, the quantity of the barium sulphate precipitated onto the substrate can be varied within wide limits, depending on the desired properties with regard to adhesive strength, extension and transparency on the skin.

As a rule, the starting suspensions contain about 10 weight percent of the flaky substrate, and the sulphate solution and the barium salt solution are added thereto as about 5-25 percent by weight solutions. Preferably, the barium salt is used in a quantity of 0.8-0.98 mol per mol of sulphate. After coating with the barium sulphate, the pigment is as a rule separated off, washed with water and dried at about 105°-110° C.

In a further embodiment of the invention, a metal oxide, hydrated metal oxide or metal carbonate is also precipitated on, in addition to the barium sulphate layer, and this additional precipitation can be either colorless or colored. In order to obtain this additional precipitation, a sulphate of a metal, which forms a sparingly soluble oxide, hydrated oxide or carbonate can be selected for the barium sulphate precipitation.

Suitable examples are titanyl sulphate, aluminum sulphate, zinc sulphate and magnesium sulphate for colorless additional precipitations, or iron (II) or iron (III) sulphate, iron ammonium sulphate, chromium sulphate, manganese sulphate or cobalt sulphate for colored additional precipitations. The precipitation can be carried out in such a way that, after the completion of the barium sulphate precipitation, a base or an alkaline carbonate solution is added to the suspension. The base used can, for example, be an aqueous solution of sodium hydroxide, potassium hydroxide, ammonium hydroxide or of a substance which gives ammonium hydroxide in aqueous solution, such as, for example, urea or acetamide. The carbonate used can, for example, be sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, ammonium carbonate or ammonium bicarbonate.

In general, a suspension of about 10 parts of the flaky substrate in about 100 parts of water at about 5°-100° C., in particular about 20°-95° C., is also used in this method, and an about 5-25 percent by weight solution of barium salt and about 1.01-2 mol, relative to the barium salt, of an aqueous metal sulphate solution, for example a titanyl sulphate solution, is added to the suspension.

After completion of the addition, an about 5-25 percent by weight solution of a base or of an alkaline carbonate solution is added with stirring, until the pH value of the suspension has been adjusted to a value of about 3-10, depending on the desired precipitation of a hydrated metal oxide or of a carbonate. As a rule, the product formed is then filtered off, washed, dried at about 105°-110° and, if appropriate, calcined.

If the additional precipitation is carried out in the manner described, the quantity of the additional precipitation is fixed by the quantity of the metal sulphate used. It is also possible, however, not to add the metal selected for the additional precipitation before the precipitation of barium sulphate, but only after the precipitation of barium sulphate. Metal salts, such as, for example, titanium tetrachloride, titanium trichloride, aluminum chloride, aluminum nitrate, zinc chloride, zinc nitrate, bismuth oxychloride, magnesium chloride, magnesium nitrate, calcium chloride, iron (II) chloride, iron

(III) chloride, iron nitrate, chromium chloride, chromium nitrate, manganese nitrate, cobalt chloride and cobalt nitrate are suitable for this purpose.

These metals are precipitated as the oxide, hydrated oxide or carbonate onto the substrate coated with barium sulphate, and this can be proved by microscopy, electron microscopy and X-ray structural analysis. Examples of metal oxides are titanium dioxide, aluminum oxide, zirconium oxide, zinc oxide, calcium oxide and magnesium oxide. Examples of hydrated oxides are hydrated titanium oxide, hydrated aluminum oxide, hydrated zirconium oxide, zinc hydroxide, calcium hydroxide and magnesium hydroxide. Examples of metal carbonates are magnesium bicarbonate, calcium bicarbonate and zinc bicarbonate.

In this case, the precipitation can be carried out immediately after the precipitation of the barium sulphate, or a pigment coated with barium sulphate can be resuspended in water for the additional precipitation. In every case, an approximately 10 percent by weight suspension is used, to which an about 2-25 percent by weight aqueous base are added at a temperature of about 5°-100° C., preferably about 20°-95°.

In the precipitation of hydrated titanium oxide, for example, it is advantageous to maintain a pH value of 1.8-2.2 during the precipitation. It is a general principle that the pH value of the suspension is adjusted such that, after the end of the reaction, the total metal has been precipitated as the hydrated oxide, oxide or carbonate. Subsequently, the pigment is as a rule separated off, washed, dried and, if appropriate, calcined. During drying and especially during calcining at temperatures of up to 8°-900° C., the corresponding oxides are formed from the hydrated oxides and, at higher temperatures, also from the carbonates.

If desired, the pigments formed can also be colored with colorants, and they can be very advantageously used together with the additives, conventional for this purpose, in face powders and similar preparations.

By using the foregoing procedures or equivalent ones, the desired firmly adhering coating will be achieved, i.e., the coating will remain on the substrate throughout the conventional use lifetime of the pigments.

In general, the amount of barium sulphate in the finally produced flaky pigment can range broadly, e.g., from 10 to 40 weight percent based on the total weight of the pigment, preferably 20 to 30 thereof. Similarly, the amount of the oxide, hydrated oxide or carbonate can range broadly, e.g., from 5 to 30 weight percent based on the total weight of the pigment, preferably 10 to 20 weight percent.

In some cases the additional amount of oxide, hydroxide or carbonate can improve the adhesion of the barium sulphate layer and/or impart some gloss to these low luster pigments. By small amounts of colored metal oxides a shade of color can be imparted to the pigments, which might be attractive for special uses.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever. In the following examples, all temperatures are set forth uncorrected in degrees Celsius; unless otherwise indicated, all parts and percentages are by weight.

EXAMPLE 1

30 g of barium chloride are dissolved at 25° C. in a suspension of 50 g of muscovite mica of a particle size of 1-15 μ m in 500 ml of water, and 200 g of a 10 percent weight sodium sulphate solution are added with stirring at a rate of 2.5 ml per minute.

After stirring for a further 20 minutes, the product is filtered off, washed with water, until chloride ions are no longer detectable, and dried for about 8 hours at 105°-110° C. The flake pigment exhibits good properties with respect to extension and adhesion on the skin. By X-ray diffraction and electron-microscopic investigation, it can be shown that fine particles of barium sulphate have been precipitated on the mica surface.

EXAMPLE 2

30 g of barium chloride are dissolved at 25° C. in a suspension of 50 g of muscovite mica of a particle size of 20-60 μ m in 500 ml of water, and 200 g of a 10 percent by weight sodium sulphate solution are allowed to run in at a rate of 2.5 ml per minute. After stirring for a further 20 minutes, the product is filtered off, washed with water, until chloride ions are no longer detectable, and dried for about 8 hours at 105°-110° C. The flake pigment exhibits good properties with respect to extension and adhesion on the skin.

EXAMPLE 3

300 ml of a 10 percent by weight barium chloride solution are added at a rate of 3.3 ml per minute and, simultaneously, 200 ml of a 10 percent by weight potassium sulphate solution are added at a rate of 2.5 ml per minute at 60° C. to a suspension of 50 g of muscovite of a particle size of 1-15 μ m in 500 ml of water. After stirring for a further 20 minutes, the product is, as in Example 1, filtered off, washed with water and dried for about 8 hours at 105°-110° C. The flake pigment exhibits good properties with respect to extension and adhesion on the skin.

EXAMPLE 4

300 ml of a 10 percent by weight barium chloride solution are added at a rate of 3.3 ml per minute and, simultaneously, 200 ml of a 10 percent by weight magnesium sulphate solution are added at a rate of 2.5 ml per minute at 25° C. to a suspension of 50 g of muscovite mica of a particle size of 1-15 μ m in 500 ml of water. The product is filtered, washed and dried as in Example 1. The flake pigment exhibits good properties with respect to extension and adhesion on the skin.

EXAMPLE 5

300 ml of a 10 percent by weight barium chloride solution, the pH value of which has been adjusted to 1.0-2.0 by the addition of concentrated hydrochloric acid, are added at a rate of 3.3 ml per minute and, simultaneously, 200 ml of a 10 percent by weight sodium sulphate solution are added at a rate of 2.5 ml per minute, at 60° C. with stirring, to a suspension of 50 g of sericite mica of a particle size of 1-20 μ m in 500 ml of water. After stirring for a further 20 minutes, the product is filtered off, washed and dried as in Example 1. The flake pigment exhibits good properties with respect to extension and adhesion on the skin.

EXAMPLE 6

300 ml of a 10 percent by weight barium chloride solution are added at a rate of 3.3 ml per minute and, simultaneously, 200 ml of a 10 percent by weight sodium sulphate solution are added at a rate of 2.5 ml per minute, at 25° C. with stirring, to a suspension of 50 g of talc of a particle size of 1-20 μ m in 500 ml of water. After stirring for a further 20 minutes, the product is filtered off, washed and dried as in Example 1.

The flake pigment exhibits good properties with respect to extension and adhesion on the skin.

EXAMPLE 7

90 ml of a 10 percent by weight aluminum sulphate solution and of a 10 percent by weight sodium hydroxide solution are added at 70° C. to a suspension of 50 g of the pigment, prepared according to Example 1, in 500 ml of water, the pH value of the suspension being maintained in the range 6.0-8.0. 2 g of Rhodamin B are dissolved in this suspension, and 25 ml of a 20 percent by weight solution of tannic acid are then added slowly. Subsequently, to complete the color lake, a 10 percent by weight solution of tartar emetic is added, until the dye has disappeared. After filtering off, washing with water and drying, a pigment corresponding to Example 1 is obtained, which additionally has a coating of a color lake.

EXAMPLE 8

300 ml of a 10 percent by weight barium chloride solution are added at a rate of 3.3 ml per minute and, simultaneously, 200 ml of a 10 percent by weight potassium sulphate solution are added at a rate of 2.5 ml per minute, at 25° C. with stirring, to a suspension of 50 g of mica of a particle size of 1-15 μ m in 500 ml of water. After stirring for a further 20 minutes, the product is filtered off, washed with water and dried as in Example 1. 50 g of the whitish product thus obtained are suspended in 500 g of water, and 280 ml of a 15 percent by weight titanium chloride solution and, simultaneously, of a 10 percent by weight sodium hydroxide solution are added at 70° C. in such a way that the pH value of the suspension is maintained at 1.8-2.0.

The product is then filtered off, washed with water, dried for about 8 hours at 105°-110° C. and calcined for 1 hour at about 800° C. The flake pigment exhibits excellent properties with respect to extension and adhesion on the skin.

EXAMPLE 9

55 g of iron ammonium sulphate, 10 g of magnesium sulphate and 80 g of urea are dissolved in a suspension of 90 g of a mica pigment, coated with barium sulphate as in Example 8, in 900 ml of water. The suspension is then heated to 95°-98° C. and stirred for 1 hour. The product thus formed is filtered off, washed with water and dried for about 8 hours at about 105°-110° C. The flake pigment has a yellow color like hydrated iron oxide and possesses outstanding properties with respect to transparency and gloss as well as good extension and adhesion on the skin.

EXAMPLE 10

The pigment prepared according to Example 9 is calcined for 1 hour at 800° C. This gives a reddish product which, according to X-ray diffraction and electron-

microscopic investigation, consists of mica with fine particles of Fe_2O_3 and barium sulphate.

EXAMPLE 11

24.4 g of barium chloride are dissolved in a suspension of 50 g of mica of a particle size of 1-15 μ m in 500 ml of water. 300 ml of a 12 percent by weight titanium sulphate solution are added with stirring to the suspension, heated to 85°-92° C., at a rate of 5 ml per minute, followed by about 150 ml of a 10 percent by weight sodium hydroxide solution to a rate of 5 ml per minute, so that the pH value at the end of the reaction is about 5.6. The product is filtered off, washed with water, dried for about 8 hours at 105°-110° C. and calcined for 1 hour at about 800° C. The adhesion properties of this product are improved as compared with a mica pigment having a barium sulphate coating.

EXAMPLE 12

Simultaneously, 300 ml of a 10 percent by weight barium chloride solution are added at a rate of 3.0 ml per minute and 340 ml of a 10 percent by weight magnesium sulphate solution are added at a rate of 3 ml per minute, with stirring, to a suspension of 50 g of mica of a particle size of 1-15 μ m in 500 ml of water. The pH value of the suspension is then adjusted to 8.0 by adding a 10 percent by weight sodium carbonate solution. The product coated with barium sulphate and magnesium carbonate is filtered off, washed with water and dried for about 8 hours at 105°-110° C. It exhibits good extension on the skin.

EXAMPLE 13

200 ml of a 10 percent by weight barium chloride solution are added at a rate of 5 ml per minute and, simultaneously, 250 ml of a 10 percent by weight zinc sulphate solution are added at a rate of 5 ml per minute, at 70° C. with stirring, to a suspension of 50 g of mica of a particle size of 1-15 μ m in 500 ml of water. The pH value of the suspension is then adjusted to 8.5 by adding a solution which contains 10 percent by weight of potassium bicarbonate and 10 percent by weight of potassium carbonate.

By filtering off, washing with water, drying at about 105°-110° C. for about 8 hours and calcining at about 650° C. for one hour, a whitish pigment with a coating of barium sulphate and zinc oxide is obtained. The pigment possesses good extension and adhesion.

EXAMPLE 14

300 ml of a 10 percent by weight barium chloride solution are added at a rate of 3 ml per minute and, simultaneously, 400 ml of 10 percent by weight iron ammonium sulphate solution are added at a rate of 4 ml per minute, at 65° C. with stirring, to a suspension of 50 g of mica of a particle size of 1-15 μ m in 500 ml of water. The pH value of the suspension is then adjusted to 7.0 by adding a 10 percent by weight potassium hydroxide solution, and the product formed is filtered off, washed with water and dried for about 8 hours at 105°-110° C. This gives a product with a layer of hydrated iron oxide and barium sulphate on mica.

EXAMPLE 15

The yellow pigment prepared according to Example 14 is calcined for 1 hour at about 800° C., a reddish pigment being obtained.

EXAMPLE 16

200 ml of a 10 percent by weight barium chloride solution are added at a rate of 5 ml per minute and, simultaneously, 200 ml of a 10 percent by weight aluminum sulphate solution are added, at 70° C. with stirring, to a suspension of 50 g of mica of a particle size of 1-15 μ m in 500 ml of water. The pH value of the suspension is then adjusted to 7.5 by adding a 10 percent potassium hydroxide solution, and the product formed is filtered off, washed with water and dried for about 8 hours at 105°-110° C. A pigment having a layer of barium sulphate and aluminum hydroxide and possessing good extension and adhesion on the skin is obtained.

EXAMPLE 17

The procedure is analogous to Example 1, but talc having a particle size of 1-20 μ m is used in place of mica.

EXAMPLE 18

A compact powder for use in make-up is prepared by mixing the following ingredients:

63.5 parts by weight of the pigment prepared according to Example 1

5.0 parts by weight of a color pigment

8.0 parts by weight of lanolinic acid

4.0 parts by weight of isopropyl myristate

2.5 parts by weight of calcium stearate

17.0 parts by weight of corn starch.

In the cosmetic thus prepared, the pigment according to this invention exhibits better properties with respect to transparency, gloss, extension and adhesion than the mica or talc used according to the state of the art.

EXAMPLE 19

A compact powder for use in make-up is prepared by mixing the following ingredients:

75.0 parts by weight of the pigment according to Example 11

3.0 parts by weight of the colored pigment according to Example 15

2.0 parts by weight of color pigment

3.0 parts by weight of lanolinic acid

3.0 parts by weight of isopropyl myristate.

2.0 parts by weight of calcium stearate

12.0 parts by weight of corn starch.

In the cosmetic thus prepared, the pigment according to the invention possesses better properties with respect to transparency, gloss, extension and adhesion than the mica or talc used according to the state of the art.

The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

What is claimed is:

1. In a powdery cosmetic composition comprising a flaky pigment and at least one other compatible ingredient, the improvement wherein the flaky pigment com-

prises a flaky pigment substrate having a firmly adhering coating of precipitated barium sulfate, and a metal oxide, hydrated metal oxide or metal carbonate compatible with the end use of the pigment, the amount of barium sulfate being effective to improve the skin adhesion capacity or extension on the skin of the powdery cosmetic composition.

2. A composition of claim 1, wherein the substrate is mica, talc or kaolin.

3. A composition of claim 1 wherein the substrate has a particle size of 1-100 μ m.

4. A composition of claim 1 wherein the amount of metal salt is about 1 to 2 moles per mole of barium salt.

5. A composition of claim 1 wherein the oxide, hydrated oxide or carbonate is of titanium, aluminum, zinc, magnesium, iron, chromium, manganese or cobalt.

6. A composition of claim 1 further comprising a compatible colorant.

7. In a facial powder comprising a flaky pigment and at least one other compatible ingredient, the improvement wherein the flaky pigment is that of claim 1.

8. A composition of claim 1, wherein the flaky pigment is prepared by treating an aqueous suspension of the flaky substrate with an aqueous solution containing barium ions and an aqueous solution containing sulfate ions, under conditions in which barium sulfate precipitates, simultaneously or after the precipitation of barium sulfate, also precipitating a metal oxide, hydrated metal oxide or metal carbonate, and then separating the resultant coated pigment.

9. A composition of claim 8, wherein the coated pigment is further dried and calcined.

10. A composition of claim 8, wherein the preparation of the flaky pigment further comprises, after the precipitation of barium sulfate, precipitating a metal oxide, hydrated metal oxide or metal carbonate, by addition of an aqueous base or an aqueous alkaline solution containing carbonate ions.

11. A composition of claim 8, wherein a metal salt of titanium, aluminum, zinc, magnesium, iron, chromium, manganese or cobalt is used for the preparation of the metal oxide, hydrated oxide or carbonate.

12. A composition of claim 10, wherein a metal salt of titanium, aluminum, zinc, magnesium, iron, chromium, manganese or cobalt is used for the precipitation of the metal oxide, hydrated oxide or carbonate.

13. A composition of claim 1, wherein in the preparation of the flaky pigment, the sulfate ions are used in stoichiometric excess over the barium ions.

14. A composition of claim 8, wherein said two aqueous solutions are added to the suspension simultaneously.

15. A composition of claim 8, wherein said two aqueous solutions are added to the suspension successively.

16. A nacreous flaky pigment, comprising a flaky pigment substrate having a firmly adhering coating of barium sulfate, the amount of the latter being effective to improve the skin adhesion capacity or extension on the skin of a cosmetic powder when the flaky pigment is used in the cosmetic powder, and wherein the flaky substrate is mica whose barium sulfate coating also comprises a metal oxide, hydrated metal oxide or metal carbonate compatible with the end use of the pigment, and which renders the pigment nacreous.

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US006310118B1

(12) **United States Patent**
Atarashi et al.(10) **Patent No.:** US 6,310,118 B1
(45) **Date of Patent:** Oct. 30, 2001(54) **COLORING MATERIAL COMPOSITION**(75) **Inventors:** Takafumi Atarashi, Tokyo; Katsuto Nakatsuka, 3-5-1403, Moniwadai 4-chome, Taihaku-ku, Sendai, Miyagi, both of (JP)(73) **Assignees:** Nittetsu Mining Co., Tokyo; Katsuto Nakatsuka, Miyagi, both of (JP)(*) **Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.(21) **Appl. No.:** 09/242,470(22) **PCT Filed:** Aug. 20, 1997(86) **PCT No.:** PCT/JP97/02096

§ 371 Date: Feb. 18, 1999

§ 102(e) Date: Feb. 18, 1999

(87) **PCT Pub. No.:** WO98/07792**PCT Pub. Date:** Feb. 26, 1998(30) **Foreign Application Priority Data**Aug. 22, 1996 (JP) 8-221498
Dec. 16, 1996 (JP) 8-335787(51) **Int. Cl.⁷** C08K 9/00(52) **U.S. Cl.** 523/205; 523/206; 523/209; 523/216(58) **Field of Search** 523/205, 206, 523/209, 216(56) **References Cited****U.S. PATENT DOCUMENTS**

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Primary Examiner—Edward J. Cain(74) *Attorney, Agent, or Firm*—Sughrue, Mion, Zinn Macpeak & Seas, PLLC(57) **ABSTRACT**

A colorant composition capable of giving a coating film excellent in heat resistance and weather resistance which not only can have a single clear color, such as, blue, green, yellow, or the like, and be used for forgery prevention based on discrimination by means other than visible light rays, but also does not suffer color fading even at a high temperature of 350° C. to 600° C. The colorant composition comprises at least a powder comprising a base particle coated with a multilayered film comprising layers differing from each other in refractive index to make the base particle have an interference color, wherein the powder is dispersed in a dispersion medium.

13 Claims, 3 Drawing Sheets

FIG. 1

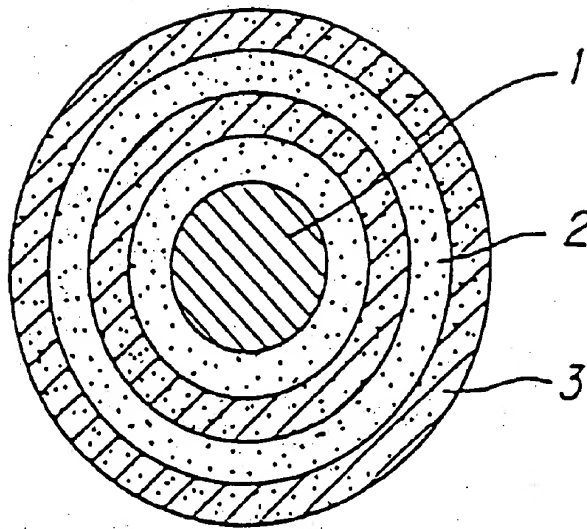


FIG. 2

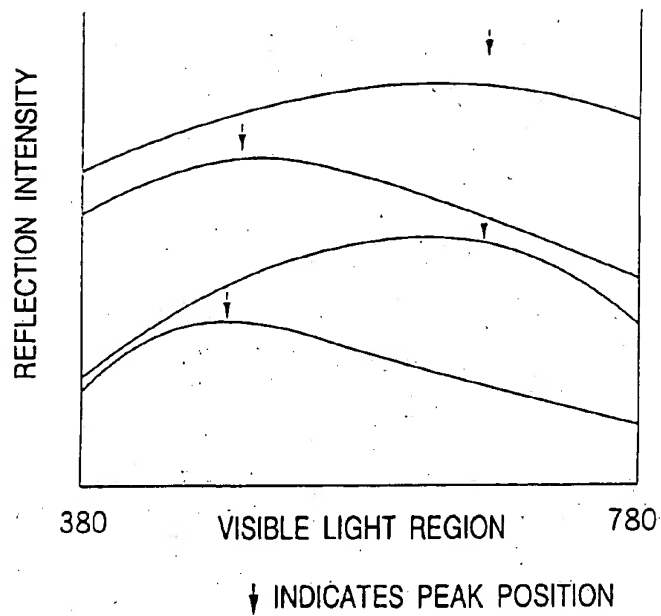


FIG. 3

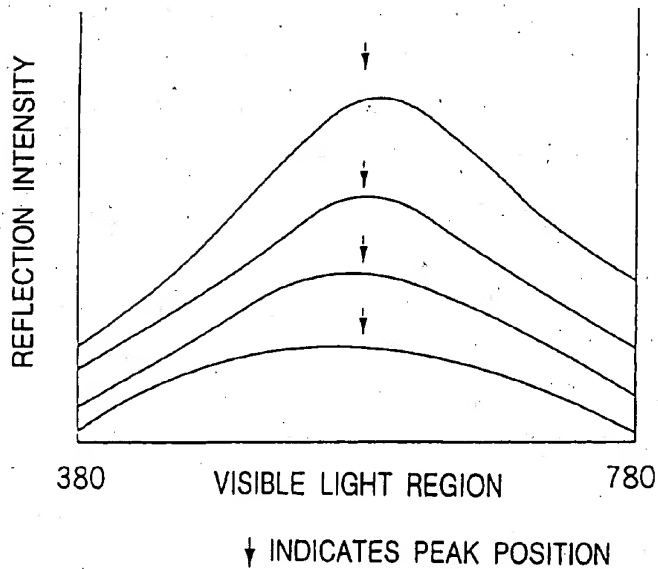
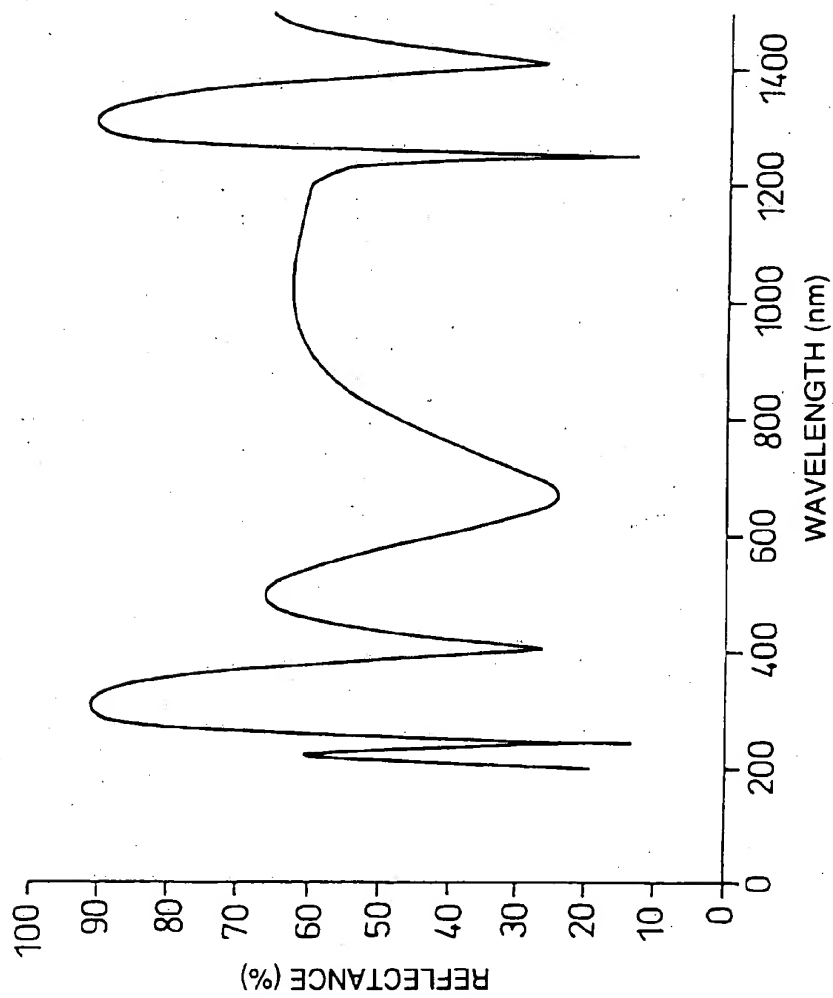


FIG. 4



COLORING MATERIAL COMPOSITION

TECHNICAL FIELD

The present invention relates to a colorant composition. More particularly, this invention relates to a heat-resistant colorant composition which is useful as an ink for color printing or holography and gives a coating film withstanding a high temperature, specifically, a colorant composition which combines heat resistance, weather resistance, and light resistance and can give a coating film withstanding a high temperature of 350° C. to 600° C. and having sufficient weather resistance and light resistance.

Furthermore, this invention relates to a colorant composition which is also applicable to a high-performance ink for magnetic color printing and is capable of heightening the effect of print forgery prevention.

BACKGROUND ART

A technique of coating a powder with another substance in order to use the powder in various applications is known. With progress in various technical fields, there is a growing desire for a powder having unique properties, especially a metal or metal compound powder. Namely, there is a desire for a powder which combines properties inherent only in a powder, especially a metal or metal compound powder, with other properties so as to have a combination of functions.

For example, in the case of a magnetic metal powder for use as a material for a magnetic color toner, the magnetic powder cannot be used if the color thereof remains as it is, although this does not arouse a problem in conventional black magnetic toners. Any conventionally known coated powder obtained by forming a thin metal oxide film on the surface of a powder for the purpose of surface modification so as to, e.g., protect the powder or facilitate mixing of the powder with, e.g., a synthetic resin does not satisfy the new requirements in such a field. From this standpoint, it is necessary to provide a powder having a novel constitution not seen in any conventional powder.

The present inventors previously invented a powder comprising a base powder particle of either a metal or a metal compound and having thereon a metal oxide film having an even thickness of 0.01 to 20 μm and in which the metal contained therein differs in kind from the metal constituting the base powder particle, in order to provide a powder which combines properties inherent only in the metal particle or metal compound particle with other properties so as to have a combination of functions (JP-A-6-228604). The present inventors further improved the above powder and invented also a powder comprising a base particle having not only a metal oxide film alone but also plural layers of a metal oxide film and a metal film alternately (JP-A-7-90310). Furthermore, the present inventors filed a patent application relating to a process which comprises similarly forming a multilayered metal oxide film on the surface of a metal or metal compound powder and subjecting the powder coated with the multilayered metal oxide film to a heat treatment to produce a powder having a denser and stabler, multilayered metal oxide film (Japanese Patent Application No. 7-80832).

For producing these powders, it is necessary to form two or more metal oxide films each having an even thickness on a base powder particle. Since it is difficult to precipitate either a metal oxide or a metal compound serving as a precursor thereof from an aqueous metal salt solution in forming such a multilayered film, the present inventors developed a method for forming a metal oxide film on a base particle of the powder by dispersing the base particles into

a metal alkoxide solution and hydrolyzing the metal alkoxide. Due to this method, it has become possible to form a metal oxide film which is thin and even in thickness and, in particular, it has become possible to form a multilayered metal oxide film.

On the other hand, in the case where a coating material is used for forming a coating film to be used in a high-temperature place, the coating material used is a heat-resistant coating material which withstands the temperature. Also, even when colorant compositions (ink/coating compositions) developed for use in applications where heat resistance or weather resistance is required are used, the coating films obtained by applying the colorant compositions generally have a low heat resistance temperature. This is attributable to the fact that the colorant compositions employ pigments which have low thermal stability at a high temperature. For example, organic pigments suffer discoloration or oxidation/combustion at a temperature not lower than 300° C. Even inorganic pigments, which have relatively high thermal stability, are apt to suffer thermal denaturation and frequently react with additives or adhesive substances to undergo discoloration or color fading. Moreover, long-term exposure to sunlight frequently results in color fading.

A colorant composition generally comprises an inorganic or organic pigment dispersed in a solvent containing dissolved therein a medium (dispersion medium) serving as a film-forming agent. However, none of the prior art pigmented coating materials contains a pigment which itself has a stable color tone at a temperature not lower than 350° C.

In heat-resistant colorant compositions, media (dispersion media) for heat-resistant coating materials have conventionally been thought to be classified by use temperature as follows: organic media and silicone-modified organic media are usable at a temperature up to about 165° C.; silicone-modified aluminum media or silicone media are usable with thermally stable coloring pigments at a temperature up to about 316° C.; silicone media and aluminum pigments are usable or silicone media and black/gray pigments are usable at a temperature up to about 424° C.; silicone media and aluminum pigments are usable at a temperature up to about 538° C.; and silicone-modified aluminum media are usable at a temperature up to about 650° C. It is further thought that at a temperature not lower than 650° C., none of such heat-resistant media is usable and ceramic coating is the only usable technique.

In the case where the film-coated powders described above are to be applied to color printing inks or the like, the powders should be colored. However, since the pigment itself suffers pulverization in a mechanochemical method and comes to have a reduced particle diameter and a lighter color, coloring with a dye or the like is necessary. This applies also to magnetic inks; since the magnetic material has a dull color, a coloring pigment or a white vehicle is added in an exceedingly large amount in order to eliminate the color, resulting in reduced magnetic properties.

In the case of color printing or magnetic color printing for producing gift checks, the demand for which is increasing recently, or producing concert tickets and the like, there are desires not only for elegant coloring and suitability for visual or magnetic reading but also for a special function for forgery prevention.

Furthermore, in production facilities used over long in a high-temperature state, such as high-temperature heat treatment apparatuses, high-temperature reactors, high-temperature dissolvers, and the like, and in general facilities and the like used over long in a high-temperature state, such

as high-temperature heaters, cooking utensils, and the like, there frequently is the necessity of coating those parts of such apparatuses and tools which are to be exposed to a high temperature for the purpose of protecting the apparatuses and tools against oxidation or enabling these to retain a beautiful appearance. There is hence a desire for a coating material which does not suffer discoloration/color fading even when exposed to a high temperature over long. In addition, a weather-resistant and light-resistant coating material is desired for the coating of facilities and tools to be used outdoors over long.

Accordingly, an object of the present invention is to eliminate these problems and provide a colorant composition which not only can be used as a color ink of a single, clear, stable color tone, such as blue, green, yellow, or the like, even without incorporation of a dye or pigment therein, but also functions to enhance a print forgery preventive performance based on a new technique other than visual examination or magnetic reading when used in combination with a reader. Another object of the present invention is to provide a colorant composition which not only has such excellent functions but also can exhibit an excellent magnetic performance also in magnetic color printing.

Still another object of the present invention is to provide a colorant composition capable of giving a coating film excellent in heat resistance and weather resistance which does not suffer color fading even at a high temperature of 350° C. to 600° C.

DISCLOSURE OF THE INVENTION

The present inventors made intensive studies. As a result, they have found that an ink having a clear stable color tone, such as blue, green, yellow, or the like, can be obtained without using a dye or pigment by forming a thin film composed of two or more layers differing in refractive index on the surface of a powder to regulate the multilayered film with respect to reflected-light interference waveform, and that this ink is effective in forgery prevention based on print discrimination with an invisible light.

It has also been found that powders having various properties, such as ferroelectric materials, conductive materials, and the like, can be utilized as the above powder, and that even when a magnetic material is used alone, it can be colored in a bright tint without impairing the magnetic properties thereof.

Furthermore, in the multilayer-coated powder invented by the present inventors, since the substances constituting the metal oxide films or metal films constituting the multilayered coating film serving as a light interference film are stable to heat, this multilayered coating film serving as a light interference film is stable to heat. The present inventors hence came to have a concept that a colorant composition (ink/coating composition) for heat-resistant applications might be obtained when the multilayer-coated powder described above was used. They pursued investigations based on that idea and, as a result, have completed the present invention.

Specifically, the present invention can accomplish the above-described objects by the following means.

- (1) A colorant composition comprising at least a powder comprising a base particle coated with a multilayered film comprising layers differing from each other in refractive index to make the base particle have an interference color, wherein the powder is dispersed in a dispersion medium.
- (2) The colorant composition as described in the above (1), wherein the base particle of the powder is a magnetic material.

- (3) The colorant composition as described in the above (1), wherein the base particle of the powder is a dielectric material.
- (4) The colorant composition as described in the above (1), wherein the base particle of the powder is a conductive material.
- (5) The colorant composition as described in the above (1), wherein the base particle of the powder is made of a material which suffers neither deformation nor discoloration at a high temperature of 350° C. to 600° C.
- (6) The colorant composition as described in the above (1) wherein at least one layer of the multilayered film of the powder is a metal compound layer.
- (7) The colorant composition as described in the above (1), wherein at least one layer of the multilayered film of the powder is a metal layer or an alloy layer.
- (8) The colorant composition as described in the above (1), wherein the powder has at least one specific interference reflection peak outside the visible light region besides in the visible light region.
- (9) The colorant composition as described in the above (1), wherein the dispersion medium comprises at least one resin and a solvent.
- (10) The colorant composition as described in (9), wherein the resin is at least one heat-resistant resin.
- (11) The colorant composition as described in (10), wherein the heat-resistant resin is at least one selected from a pure silicone resin, a fluororesin, and a silicone-modified resin.
- (12) A color ink composition comprising the colorant composition as described in the above (1).
- (13) A heat-resistant colorant composition comprising the colorant composition as described in the above (1).

In the present invention, light-interference coating layers made of two or more metal compounds or metals differing in refractive index are superposed on the surface of base powder particle. In this superposition, the function of reflecting or absorbing incident light in a specific wavelength range can be imparted by regulating the thickness of each film or varying the order of superposition or layer combination. Thus, the base particle can be colored in a single clear tint, such as blue, green, yellow, or the like, and can be made to have one or more specific interference reflection peaks outside the visible light region besides in the visible light region. In addition, the thus-colored powder undergoes no color change as long as the shape of the base particle of the powder or the refractive index or thickness of each layer of the multilayered film does not change considerably with changing temperature. Since the refractive index and thickness of each layer change only slight, the color remains unchanged up to a high temperature. Consequently, a stable color is maintained at a high temperature of 350° C. to 600° C.

Furthermore, even upon long-term exposure to sunlight, the powder of the present invention suffers no color change because the shape of the base particle of the powder and the refractive index and thickness of each layer of the multilayered film do not change upon the exposure.

The powder therefore has an excellent advantage that in the case where the retention of heat resistance is especially required, this can be attained by merely using a base particle made of a metal oxide or elemental metal which each generally has high thermal stability, and there is no need of using a color substance (dye or organic pigment) having low thermal or chemical stability.

The present invention will be explained below in detail. The base particle of the multilayer-coated powder for use in the present invention is not particularly limited, and

powders having various properties, such as magnetic, ferroelectric, conductive properties, and the like, can be used. Although the base in this case has a specific gravity of 0.1 to 10.5, the specific gravity thereof is preferably 0.1 to 5.5, more preferably 0.1 to 2.8, from the standpoint of flowability and suspensibility in a dispersion medium. Specific gravities of the base smaller than 0.1 are uneconomical in that the buoyancy of the base in a dispersion medium is so high that a film composed of a larger number of layers or having an exceedingly large thickness should be formed. On the other hand, specific gravities thereof exceeding 10.5 are unsuitable in that a film for suspending the base in a dispersion medium should be formed thickly.

Materials of various kinds can be used, such as metals, metal compounds, organic substances, inorganic substances, and the like.

The metals may be any metals, such as iron, nickel, chromium, titanium, aluminum, and the like. However, in producing a powder whose magnetic properties are to be utilized, a metal capable of retaining magnetic properties, e.g., iron, is preferred. These metals may be alloys. In the case where the magnetic powder is to be produced, it is preferred to use a ferromagnetic alloy. Typical metal compounds include oxides of the aforementioned metals. Although examples thereof include oxides of iron, nickel, chromium, titanium, aluminum, and silicon, the metal compounds may also be oxides of calcium, magnesium, barium, and the like, or may be composite oxides thereof. Furthermore, examples of metal compounds other than metal oxides include metal nitrides, metal carbides, metal sulfides, metal fluorides, metal carbonates, and metal phosphates. Specifically, iron nitride and the like are preferred.

The organic substances are preferably resin particles. Examples thereof include cellulose powders, cellulose acetate powders, polyamides, epoxy resins, polyesters, melamine resins, polyurethanes, vinyl acetate resins, silicone resins, and spherical or pulverized particles obtained through the polymerization or copolymerization of acrylic esters, methacrylic esters, styrene, ethylene, propylene, and derivatives thereof. Especially preferred resin particles are spherical acrylic resin particles obtained by the polymerization of an acrylic or methacrylic ester.

Usable as the inorganic substances are inorganic hollow particles, such as Shirasu balloons (hollow silicic acid particles) and the like, fine hollow carbon spheres (Kureca Sphere), fused alumina bubbles, aerosil, white carbon, fine hollow silica spheres, fine hollow calcium carbonate spheres, calcium carbonate, pearlite, talc, bentonite, micas, such as synthetic micas, common mica, and the like, kaolin, and the like.

The material for use as the base to be coated with a multilayered film is preferably a metal, especially preferably iron or an iron-based alloy, for example, for use in applications, such as automotive coating, steel can printing, and the like. Likewise in the case of printing on aluminum products, such as aluminum cans and the like, it is especially preferred to use aluminum as the base. This is because the multilayered film and the base are thought to be more effective in hiding the color of the article to be coated or printed, when the article is made of the same material as the base.

Examples of the shape of the base powder particle include isotropic shapes, such as sphere, nearly spherical shapes, regular polyhedrons, and the like, and polyhedrons, such as rectangular parallelepipeds, spheroids, rhombohedrons, plates, acicular shapes (cylinders and prisms), and the like. Also usable are powders of completely irregular shapes, such as pulverized particles and the like.

In the present invention, the base powder particle constituting the core of the powder may be an organic substance or an inorganic substance as described above. However, especially in the case where the powder is required not to suffer deformation or discoloration at a high temperature of 350° C. to 600° C., inorganic substances are preferred, and a very limited number of organic substances are usable.

The apparent specific gravity of the base powder particle in this case is not particularly limited. For a colorant (coating material) having a low viscosity, it is preferred to use a base powder particle having a small apparent specific gravity close to that of the organic solvent serving as a dispersion medium so as to impart satisfactory dispersion stability to the powder to be dispersed into the dispersion medium.

In the case of using a base particle which suffer neither deformation nor discoloration at a high temperature, examples of the inorganic substance constituting the base particle include metals, such as iron, nickel, chromium, titanium, aluminum, and the like, metal alloys, such as iron-nickel and iron-cobalt alloys, iron-nickel alloy nitrides, iron-nickel-cobalt alloy nitrides, and the like, and further include various inorganic compounds, examples of which include metal oxides, such as oxides of iron, nickel, chromium, titanium, aluminum, silicon (in this case, silicon is classified in metals), and the like, oxides of alkaline earth metals, such as calcium, magnesium, barium, and the like, composite oxides thereof, clays, and glasses. Examples of base powder particle having an especially small apparent specific gravity include inorganic hollow particles, such as Shirasu balloons (hollow silicic acid particles), fine hollow carbon spheres (Kureca Sphere), fine hollow silica spheres, fine hollow calcium carbonate spheres, and the like.

Although the base particle which suffers neither deformation nor discoloration at a high temperature can be made of an organic substance, many natural and synthetic polymeric compounds are unusable because they deform or oxidatively discolor upon exposure to a high temperature not lower than 350° C. (not higher than 600° C.). However, polymers suitable for the use can be found from crosslinked, heat-resistant condensation polymer compounds, e.g., polyamide resins, polyimide resins, epoxy resins, and melamine resins.

In the present invention, the base powder particle is coated with two or more coating layers which differ from each other in refractive index and which each has a suitably selected refractive index and a suitably selected thickness, whereby a powder is obtained which has an interference color and has one or more specific interference reflection peaks outside the visible light region besides in the visible light region.

The material for constituting each coating layer is preferably selected freely from inorganic metal compounds, metals or alloys, and organic substances.

Typical examples of the inorganic metal compounds which may constitute the coating layers include metal oxides. Specific examples thereof include oxides of iron, nickel, chromium, titanium, aluminum, silicon, calcium, magnesium, and barium and composite oxides thereof, such as barium titanate, lead titanate, and the like. Examples of the metal compounds other than metal oxides include metal fluorides, such as magnesium fluoride, calcium fluoride and the like, metal nitrides such as iron nitride and the like, metal sulfides such as zinc sulfide, cadmium sulfide and the like, metal carbonates, such as calcium carbonate and the like, metal phosphates, such as calcium phosphate and the like, and metal carbides.

Examples of the elemental metals which may constitute the coating layers include silver metal, cobalt metal, nickel

metal, and iron metal. Examples of the metal alloys include iron-nickel alloys, iron-cobalt alloys, iron-nickel alloy nitrides, and iron-nickel-cobalt alloy nitrides.

The organic substances which may constitute the coating layers are not particularly limited, and either the same organic substance as that constituting the cores or a different organic substance may be used. However, resins are preferred. Examples of the resins include cellulose, cellulose acetate, polyamides, epoxy resins, polyesters, melamine resins, polyurethane resins, vinyl resins, silicone resins, and polymers or copolymers of acrylic esters, methacrylic esters, styrene, ethylene, propylene, and derivatives thereof.

Although various materials can be used to constitute the coating layers, a suitable combination of materials should be selected according to applications while taking account of the refractive index of each coating layer.

In order for the powder for use in the heat-resistant colorant composition of the present invention to be heat-resistant, both the base powder particle and the light-interference multilayered film covering the surface of the base powder particle should suffer neither deformation nor discoloration even when kept in a high-temperature state over long. In order for the base particle and the multilayered film not to suffer deformation in a high-temperature state, the resins enumerated above as examples of the organic substances should be prevented from deforming, for example, by crosslinking. Preferred is a resin which in itself is so stable as to suffer neither decomposition nor denaturation even without crosslinking. Examples of such a preferred resin include pure silicone resins, fluororesins, and silicone-modified resins.

The coefficient of thermal volume expansion of the base particle of the heat-resistant powder is about $10^{-4}/K^{-1}$, that of the heat-resistant organic coating films is about $10^{-4}/K^{-1}$ and that of the inorganic coating films is about $10^{-5}/K^{-1}$. In addition, the thermal expansion of the base particle of the powder and that of each coating layer are relative changes. Therefore, even when such a degree of dimensional change occurs, the powder colored by the formation of a light-interference multilayered film suffers no color change.

The particle diameter of the powder according to the present invention is not particularly limited, and can be suitably regulated according to purposes. However, the diameter thereof is generally in the range of $0.01 \mu m$ to several millimeters.

The unit coating layers constituting the two or more coating layers are ones whose thicknesses have been determined so that these layers have interference reflection peaks or interference transmission bottoms at the same specific wavelength. More preferably, the thickness of each unit coating layer is determined by fixing the basic film thickness thereof which satisfies the following equation (1):

$$N \cdot d = m \cdot \lambda / 4 \quad (1)$$

[wherein N represents a complex refractive index; d represents a basic film thickness; m represents an integer (natural number); λ represents a wavelength at which an interference reflection peak or interference transmission peak appears; and N is defined by the following equation (2):

$$\bar{N} = n + i\kappa \quad (2)$$

(wherein n represents a refractive index of each unit coating layer; i represents a complex number; and κ represents an extinction coefficient), and correcting the actual thicknesses of the unit coating layers based on the functions consisting of the phase shift caused by the extinction coefficient κ of the

refractive index, the phase shift occurring at film interfaces, and the peak shift attributable to refractive index dispersion and particle shape so that the unit coating layers have interference reflection peaks or interference transmission bottoms at the same specific wavelength as shown above.

For forming these films, the following methods may be used according to the substances to be deposited. However, other methods can be used.

(1) Formation of Organic Substance Film (Resin Film):

a. Polymerization in Liquid Phase

Use can be made, for example, of a method in which particles serving as cores are dispersed and emulsion polymerization is conducted to form a resin film on each particle.

b. Film Formation in Vapor Phase (CVD) (PVD)

(2) Formation of Inorganic Metal Compound Film:

a. Solid Deposition in Liquid Phase

A preferred method is to disperse particles serving as cores into a metal alkoxide solution and hydrolyze the metal alkoxide to thereby form a metal oxide film on each particle. This method can form a dense metal oxide film. It is also possible to react an aqueous solution of a metal salt to thereby form a film of a metal oxide or the like on particles.

b. Film Formation in Vapor Phase (CVD) (PVD)

(3) Formation of Metal Film or Alloy Film:

a. Reduction of Metal Salt in Liquid Phase

Use is made of the so-called chemical plating method in which the metal salt contained in an aqueous metal salt solution is reduced to deposit the metal to thereby form a metal film.

b. Film Formation in Vapor Phase (CVD) (PVD)

A metal film can be formed on the surface of particles, for example, by the vapor deposition of a metal.

A method for forming a multilayered film composed of layers of a metal oxide having a high refractive index and, alternately arranged therewith, layers of a metal oxide having a low refractive index is explained below in detail as an example. First, base powder particles are dispersed into an alcohol solution of an alkoxide of titanium, zirconium, and the like. A mixed solution consisting of water, an alcohol, and a catalyst is added dropwise to the dispersion with stirring to hydrolyze the alkoxide to thereby form on the surface of each base powder particle a film of titanium oxide or zirconium oxide as a high-refractive-index film. Thereafter, this powder is taken out by solid/liquid separation, dried, and then subjected to a heat treatment. The drying may be conducted by any means selected from vacuum drying with heating, vacuum drying, and natural drying. It is also possible to use an apparatus, such as a spray dryer or the like, in an inert atmosphere while regulating the atmosphere. The heat treatment may be accomplished by heating the powder at 150 to $1,100^\circ C$. (when the base powder particles are inorganic particles) or at 150 to $500^\circ C$. (when the base powder particles are not inorganic particles) for from 1 minute to 3 hours either in air when the film composition does not undergo oxidation or in an inert atmosphere when the film composition is susceptible to oxidation. Subsequently, the particles having the high-refractive-index film formed thereon are dispersed into an alcohol solution of a metal alkoxide which gives an oxide having a low refractive index, such as a silicon alkoxide, aluminum alkoxide, or the like. A mixed solution consisting of water, an alcohol, and a catalyst is added dropwise to the resultant dispersion with stirring to hydrolyze the alkoxide to thereby form over the surface of each base powder particle a film of silicon oxide or aluminum oxide as a low-refractive-index film. Thereafter, the powder is taken out by solid/liquid separation, vacuum-dried, and then heat-

treated in the same manner as the above. As a result of the above procedure, a high-refractive-index metal oxide film and a low-refractive-index metal oxide film are alternately formed on the surface of the base powder particles. By repeating this procedure for forming metal oxide films, a powder in each particle which has a multilayered metal oxide film on its surface is obtained.

The present invention will be explained below in more detail by reference to drawings. FIG. 1 is a sectional view diagrammatically illustrating the structure of a particle of a multilayer-coated powder for use in the colorant composition of the present invention. The particle comprises a base powder particle 1 as a core and, formed on the surface thereof, two coating layers 2 and two coating layers 3 differing in refractive index from the layers 2.

Coating films differing in refractive index are alternately formed on the surface of each base powder particle so as to satisfy the following equation (3). Namely, films which each is made of a substance having a refractive index n and has a thickness d corresponding to m (integer) times the value which is one-fourth a wavelength of visible light are formed in an appropriate thickness and number. As a result, the light having a specific wavelength λ (the light utilizing Fresnel's interference reflection) is reflected or absorbed.

$$nd=m\lambda/4$$

(3)

This function is utilized as follows. A film having such a thickness and refractive index as to satisfy equation (3) with respect to both a target wavelength of visible light and a target wavelength outside the visible light region is formed on the surface of each base powder particle, and this film is coated with a film having a different refractive index. This procedure is conducted once or repeated one or more times to thereby form films which have a characteristic reflection or absorption wavelength width both in the visible light region and outside a visible region. In the above procedure, the order of material deposition for film formation is determined in the following manner. When the base powder particles themselves have a high refractive index, a film having a low refractive index is preferably formed as the first layer. In the reverse case, a film having a high refractive index is preferably formed as the first layer.

Film thickness is controlled based on a measurement in which the change of optical film thickness, which is the product of the refractive index of the film and the film thickness, is determined as a reflection waveform with a spectrophotometer or the like. The thickness of each layer is designed so that the reflection waveform conforms to the finally required waveform. For example, in the case where the unit coating films constituting a multilayered film have reflection waveform peaks at different positions as shown in FIG. 2, the powder is white. In contrast, when the unit coating films are regulated so that the reflection waveform peaks thereof are in exactly the same position as shown in FIG. 3, a monochromatically colored powder, e.g., a blue, green, or yellow powder, can be obtained without using a dye or pigment. In addition, the powder has one or more specific interference reflection peaks also outside the visible light region.

However, in the case of an actual powder, a design should be made while taking account of the particle diameter and shape of the powder, the phase shift occurring at interfaces between film materials and the base particle material, the peak shift attributable to the wavelength dependence of the refractive index, etc. For example, in the case where the base particles have a plane parallel plate shape, the Fresnel interference caused by parallel films formed on a plane

surface of the particle is designed under the conditions including the above equation (3) in which n has been replaced with N defined by the following equation (4). In particular, in the case where a metal film is contained, extinction coefficient κ is included in the refractive index N of the metal defined by equation (4) even though the particle shape is a plane parallel plate shape. In the case of transparent oxides (dielectrics), κ is exceedingly small and negligible.

$$N=n+ik \quad (i \text{ represents a complex number}) \quad (4)$$

When the extinction coefficient κ is large, an enhanced phase shift occurs at the interface between the film material and the base particle material, and this phase shift influences the optimum interference thicknesses of all layers of the multilayered film.

Because of the above, the mere regulation of geometrical film thicknesses results in different peak positions and, hence, in a lighter color especially in monochromatic coloring. In order to avoid this, a design is made beforehand through a computer simulation so as to result in an optimal combination of film thicknesses while taking account of influences of the phase shift on all films.

Also, there are the phase shift caused by an oxide layer present on a metal surface and the peak shift attributable to the wavelength dependence of refractive index. In order to correct these, it is necessary to use a spectrophotometer or the like to find optimal conditions under which reflection peaks or absorption bottoms appear at target wavelengths in a final target number of films.

In a film formed on a curved surface such as that of a spherical particle or the like, interference occurs similarly to that on plane plates and is basically in accordance with Fresnel's interference principle. Consequently, a coloring method can be designed so as to produce a monochromatic powder as shown in FIG. 3. However, in the case of curved surfaces, the light which has struck on the powder and has been reflected causes complicated interference. The resultant interference waveforms are almost the same as on plane plates when the number of films is small. However, as the total number of films increases, the interference within the multilayered film becomes more complicated. In the case of a multilayered film also, a spectral reflection curve can be designed beforehand based on Fresnel interference through a computer simulation so as to result in an optimal combination of film thicknesses. In particular, in the case where coating films are formed on the surface of a base powder particle, the influences of a phase shift on the base powder particle surface and on all films are taken in account when a design is made beforehand through a computer simulation so as to result in an optimal combination of film thicknesses. Furthermore, the peak shift caused by a coating layer present on the base powder particle surface and the peak shift attributable to the wavelength dependence of the refractive index are also taken in account. In the actual production of a sample, designed spectral curves are referred to and, in order to correct these in actual films, it is necessary to use a spectrophotometer or the like, while changing film thicknesses, to find optimal conditions under which reflection peaks or absorption bottoms appear at target wavelengths in a final target number of films. Also in the case where a powder having irregular particle shapes is colored, interference occurs due to the multilayered film. A basic film design is hence made with reference to conditions for an interference multilayered film for spherical particles. The peak position for each of the unit coating films constituting

the multilayered film can be regulated by changing the thickness of the layer, and the film thickness can be regulated by changing the solution composition, reaction time, and the number of starting-material addition times. Thus, the powder can be colored in a desired tint. As described above, a monochromatic powder can be obtained by finding optimal conditions under which reflection peaks or absorption bottoms appear at target wavelengths in a final target number of films, while changing film-forming conditions, such as solutions for film formation and the like. Furthermore, by controlling a combination of materials for forming a multilayered film and the thicknesses of the unit coating films, the color development by interference in the multilayered film can be regulated. Thus, a powder can be colored in a desired bright tint without using a dye or pigment.

A method for preparing a colorant composition (ink/coating composition) of the present invention using the thus-obtained powder according to the present invention will be explained next.

A dispersion medium for inks which is usable in the present invention is a conventionally known varnish for use in color printing or magnetic color printing. For example, a liquid polymer, a polymer or monomer dissolved in an organic solvent (referred to also as "solvent"), or the like can be suitably selected and used according to the kind of the powder, the method of applying the ink, and the use thereof.

Examples of the liquid polymer include dienes, such as polypentadiene, polybutadiene, and the like, polyethylene glycols, polyamides, polypropylenes, waxes, and copolymers, and modifications thereof.

Examples of the polymer to be dissolved in an organic solvent include olefin polymers, acrylic resins, such as oligoester acrylates and the like, polyesters, polyamides, polyisocyanates, amino resins, xylene resins, ketone resins, diene resins, rosin-modified phenolic resins, diene rubbers, chloroprene resins, waxes, and modifications, and copolymers thereof.

Examples of the monomer to be dissolved in an organic solvent include styrene, ethylene, butadiene, and propylene.

A heat-resistant colorant composition of the present invention is prepared by mixing the powder which has been colored by forming a light-interference multilayered film composed of two or more layers differing in refractive index on a base powder particle with a heat-resistant resin, a solvent, a drying accelerator, and the like.

Examples of the heat-resistant resin for use in the heat-resistant colorant composition of the present invention include pure silicone resins and fluororesins, and further include resins obtained by modifying resins for general coating materials, such as alkyd resins, epoxy resins, urethane resins, acrylic resins, melamine resins, and the like, with a silicone to impart heat resistance thereto.

The solvent for use in the colorant composition of the present invention can be a solvent for general coating materials, and is not particularly limited. Examples of the solvent generally used for coating materials include hydrocarbon solvents, such as benzene, toluene, xylene, n-hexane, cyclohexane, benzine, kerosene, and the like, alcoholic solvents, such as methanol, ethanol, isopropanol, butanol, and the like, ketone solvents, such as acetone, MEK, methyl isobutyl ketone, and the like, and ester solvents, such as methyl acetate, ethyl acetate, butyl acetate, and the like.

Examples of the drying accelerator include lead octylate, silane coupling agents, and titanium coupling agents.

Besides the above ingredients, the colorant composition of the present invention can further contain other ingredients, such as an oil-soluble dye as a coloring agent or

toning agent, a thickening agent for increasing viscosity, a fluidizing agent for reducing viscosity, a dispersant for dispersing particles, and the like.

The colorant composition of the present invention, which employs a single powder or a combination of two or more powders differing in spectral characteristics, is accordingly applicable to color printing or magnetic color printing. In addition, when powders of the three primary colors are employed, the colorant composition is applicable to holography by a method based on the two-light-flux interference method, such as those described in JP-A-60-156004 and JP-A-2-72319. Furthermore, the colorant composition is applicable to other applications, such as a magnetic color ink for forgery prevention and the like, in which reflection in the infrared wavelength region or ultraviolet wavelength region is detected.

In the case where the above-described colorant composition of the present invention is printed or applied on a substrate or a body to be coated, the relationship between the contents of the powder and the dispersion medium in the colorant composition is such that the ratio therebetween is 1:0.5 to 1:15 by volume. If the content of the dispersion medium is too low, the film deposited does not tenaciously adhere to the body to be coated. If it is too high, the coating material is unsatisfactory in that its color is too light.

The relationship between the sum of the powder and the dispersion medium and the amount of the solvent in the colorant composition is such that the ratio therebetween is 1:0.5 to 1:10 by volume. If the amount of the solvent is too small, the coating material has too high a viscosity to be evenly applied. If the solvent amount is too large, much time is required for the coating film to dry, resulting in a considerably reduced coating efficiency.

The color density of a coating film formed by applying the colorant to a body to be coated is determined by the amount of the colored powder deposited per unit area of the body to be coated. A satisfactory coating color is obtained when the amount of the multilayer-coated powder of the present invention deposited on the body to be coated is 10 to 150 g in terms of areal density per square meter in the coating material after drying. If the areal density thereof is below the above values, the color of the body to be coated is visible. Areal densities thereof exceeding the above values are uneconomical because the color density of the coating does not change any more. Namely, even when the powder is deposited in a thickness larger than a given value on the body to be coated, light does not reach powder particles located on the lower side of the coating film. Forming a coating film in a thickness larger than such a value is uneconomical since it does not enhance the effect of coating because that thickness exceeds the hiding power of the coating material. However, this does not apply in the case where the coating material is applied thickly while taking account of the decrease in coating film thickness caused by wearing.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a sectional view diagrammatically illustrating the structure of a particle of a multilayer-coated powder for use in the colorant composition of the present invention; numeral 1 denotes a base powder particle and numerals 2 and 3 each denotes a coating layer.

FIG. 2 is a graphic presentation showing reflection intensity spectral waveforms for the unit coating films constituting the multilayered film of a powder colored in white.

FIG. 3 is a graphic presentation showing reflection intensity spectral waveforms for the unit coating films constituting the multilayered film of a powder colored monochromatically.

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FIG. 4 is a graphic presentation showing a spectral reflectance curve of the colorant composition obtained in Example 2.

BEST MODES FOR CARRYING OUT THE INVENTION

The present invention will be explained below in more detail by reference to Examples. However, the invention should not be construed as being limited to these Examples only.

Example 1

Colorant Composition 1 Employing Magnetic Material
First Layer: Silica Coating

Into 100 ml of ethanol was dispersed 10 g of a carbonyl iron powder (average particle diameter, 1.8 μm ; magnetization at 10 kOe, 203 emu/g) manufactured by BASF. The container was heated with an oil bath to keep the temperature of the liquid at 55° C. Thereto were added 6 g of silicon ethoxide, 8 g of ammonia water (29%), and 8 g of water. This mixture was reacted for 2 hours with stirring. After the reaction, the reaction mixture was diluted and washed with ethanol and filtered. The solid matter was dried in a vacuum dryer at 110° C. for 3 hours. After the drying, the resultant powder was heated with a rotary tubular oven at 650° C. for 30 minutes to obtain a silica-coated powder A₁. The film thickness of the silica coating film obtained was 98 nm. This powder was excellent in dispersed state.

Second Layer: Titania Coating

After the heating, 10 g of the silica-coated powder A₁ obtained was redispersed into 200 ml of ethanol. The container was heated with an oil bath to keep the temperature of the liquid at 55° C. Thereto was added 4.7 g of titanium ethoxide. This mixture was stirred. A solution prepared by mixing 30 ml of ethanol with 8.0 g of water was added dropwise to the above mixture over 60 minutes, and the resultant mixture was reacted for 2 hours. The particles were then vacuum-dried and heated to obtain a titania/silica-coated powder A₂. The titania/silica-coated powder A₂ obtained had satisfactory dispersibility and was composed of independent particles. The titania film of this titania/silica-coated powder A₂ had a thickness of 77 nm.

This powder had a spectral reflection curve having a peak wavelength of 410 nm and had a reflectance at the peak wavelength of 35%. It was bright-green.

This powder had a magnetization of 167 emu/g at 10 kOe.

With respect to each coating film of the above coated powder, the peak wavelength for a spectral reflection curve, the reflectance at the peak wavelength, and the refractive index and thickness of the coating film were measured by the following methods.

- (1) The spectral reflection curve was obtained by a method in which a spectrophotometer having an integrating sphere and manufactured by Nippon Bunko was used to examine light reflected by a powder sample packed in a glass holder. The examination was made in accordance with JIS Z8722 (1988) and JIS Z8723 (1988).
- (2) The refractive index and the film thickness were determined and evaluated by examining samples produced under different conditions and having large film thicknesses to obtain spectral reflection curves and comparing the examination results, for fitting, with Curves obtained through instrumental calculation based on the interference equation.

Third Layer: Silica Coating

Into 100 ml of ethanol was dispersed 10 g of the titania/silica-coated powder A₂. The container was heated with an

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oil bath to keep the temperature of the liquid at 55° C. Thereto were added 6 g of silicon ethoxide, 8 g of ammonia water (29%), and 8 g of water. This mixture was reacted for 2 hours with stirring. After the reaction, the reaction mixture was diluted and washed with ethanol and filtered. The solid matter was dried in a vacuum dryer at 110° C. for 3 hours. After the drying, the resultant powder was heated with a rotary tubular oven at 650° C. for 30 minutes to obtain a silica/titania-coated powder A₃. The film thickness of the silica/titania-coated powder A₃ obtained was 99 nm. This powder was excellent in dispersed state.

Fourth Layer: Titania Coating

After the heating, 10 g of the silica/titania-coated powder A₃ obtained was redispersed into 200 ml of ethanol. The container was heated with an oil bath to keep the temperature of the liquid at 55° C. Thereto was added 5.3 g of titanium ethoxide. This mixture was stirred. A solution prepared by mixing 30 ml of ethanol with 8.0 g of water was added dropwise to the above mixture over 60 minutes, and the resultant mixture was reacted for 2 hours. The particles were then vacuum-dried and heated to obtain a titania/silica-coated powder A₄. The titania/silica-coated powder A₄ obtained had satisfactory dispersibility and was composed of independent particles. The titania film of this titania/silica-coated powder A₄ had a thickness of 75 nm.

This powder had a reflection peak at 553 nm and a reflectance of 47%. It was bright-green.

This powder had a magnetization of 146 emu/g at 10 kOe. Preparation of Colorant Composition and Spectral Characteristics

The powder thus obtained was mixed in an amount of 65 parts with 35 parts of a polyester resin varnish.

The resultant composition was applied to a white paper with a blade coater.

The coated paper in the visible light region had a reflection peak at 553 nm with a reflectance of 53%. Outside the visible light region, the coated paper had a reflection peak at 303 nm in the ultraviolet region with a reflectance of 94%, and further had reflection peaks at 1,310 nm and 980 nm in the infrared region with reflectances of 95% and 61%, respectively.

Comparative Example 1

Mere Mixture of Magnetic Material and Pigment

Viridian (green pigment) (average particle diameter, 0.1 μm ; reflection peak, 553 nm; reflectance, 49%) was mixed with a carbonyl iron powder (average particle diameter, 1.8 μm ; magnetization at 10 kOe, 203 emu/g) manufactured by BASF, in a weight ratio of 25 g/25 g, and further with 25 g of titanium oxide (rutile; average particle diameter, 0.2 μm) as a vehicle. This mixture was sufficiently homogenized. This powder mixture had a magnetization of 67 emu/g in a magnetic field of 10 kOe.

As in the above, 65 parts of the mixed powder was mixed with 35 parts of a polyester resin varnish, and the resultant composition was applied to a white paper with a blade coater.

The paper coated with this ink had a reflection peak at 557 nm, at which the reflectance was as low as 18%.

The mere mixing of a pigment with a magnetic powder, a resin, and a solvent as in Comparative Example 1 does not result in an improved color. In order to obtain a magnetic color ink having the same magnetization, it is necessary to positively color a magnetic material as in the Example.

Example 2

Colorant Composition 2 Employing Magnetic Material
First Layer: Silica Coating

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Into an ethanol solution prepared beforehand by dissolving 3.0 g of silicon ethoxide in 158.6 g of ethanol was dispersed 20 g of a carbonyl iron powder (average particle diameter, 1.8 μm ; magnetization at 10 kOe, 203 emu/g) manufactured by BASF. Thereafter, a solution prepared beforehand by mixing 8.0 g of ammonia water with 8.0 g of deionized water was added to the dispersion with stirring. After the addition, the resultant mixture was reacted at ordinary temperature for 5 hours. The particles were washed with a sufficient amount of ethanol, subsequently vacuum-dried, and then heated with a rotary tubular oven at 500° C. for 30 minutes in a nitrogen atmosphere to obtain a silica-coated carbonyl iron powder B₁.

Second Layer: Titania Coating

Into an ethanol solution prepared beforehand by dissolving 3.0 g of titanium ethoxide in 198.3 g of ethanol was dispersed 20 g of the silica-coated carbonyl iron powder B₁. Thereafter, a solution prepared beforehand by mixing 3.0 g of deionized water with 23.7 g of ethanol was added dropwise to the dispersion with stirring over 1 hour. After the addition, the resultant mixture was reacted at ordinary temperature for 5 hours. The particles were washed with a sufficient amount of ethanol, subsequently vacuum-dried, and then heated with a rotary tubular oven at 500° C. for 30 minutes in a nitrogen atmosphere to obtain a titania/silica-coated carbonyl iron powder B₂.

Third Layer: Silica Coating

Into an ethanol solution prepared beforehand by dissolving 3.0 g of silicon ethoxide in 158.6 g of ethanol was dispersed 20 g of the titania/silica-coated carbonyl iron powder B₂. Thereafter, a solution prepared beforehand by mixing 8.0 g of ammonia water with 8.0 g of deionized water was added to the dispersion with stirring. After the addition, the resultant mixture was reacted at ordinary temperature for 5 hours. The particles were washed with a sufficient amount of ethanol, subsequently vacuum-dried, and then heated with a rotary tubular oven at 500° C. for 30 minutes in a nitrogen atmosphere to obtain a silica/titania-coated carbonyl iron powder B₃.

Fourth Layer: Titania Coating

Into an ethanol solution prepared beforehand by dissolving 3.0 g of titanium ethoxide in 198.3 g of ethanol was dispersed 20 g of the silica/titania-coated carbonyl iron powder B₃. Thereafter, a solution prepared beforehand by mixing 3.0 g of deionized water with 23.7 g of ethanol was added dropwise to the dispersion with stirring over 1 hour. After the addition, the resultant mixture was reacted at ordinary temperature for 5 hours. The particles were washed with a sufficient amount of ethanol, subsequently vacuum-dried, and then heated with a rotary tubular oven at 500° C. for 30 minutes in a nitrogen atmosphere to obtain a titania/silica-coated carbonyl iron powder B₄.

Fifth Layer: Silica Coating

Into an ethanol solution prepared beforehand by dissolving 3.0 g of silicon ethoxide in 158.6 g of ethanol was dispersed 20 g of the titania/silica-coated carbonyl iron powder B₄. Thereafter, a solution prepared beforehand by mixing 8.0 g of ammonia water with 8.0 g of deionized water was added to the dispersion with stirring. After the addition, the resultant mixture was reacted at ordinary temperature for 5 hours. The particles were washed with a sufficient amount of ethanol, subsequently vacuum-dried, and then heated with a rotary tubular oven at 500° C. for 30 minutes in a nitrogen atmosphere to obtain a silica/titania-coated carbonyl iron powder B₅.

Sixth Layer: Titania Coating

Into an ethanol solution prepared beforehand by dissolving 3.0 g of titanium ethoxide in 198.3 g of ethanol was

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dispersed 20 g of the silica/titania-coated carbonyl iron powder B₅. Thereafter, a solution prepared beforehand by mixing 3.0 g of deionized water with 23.7 g of ethanol was added dropwise to the dispersion with stirring over 1 hour. After the addition, the resultant mixture was reacted at ordinary temperature for 5 hours. The particles were washed with a sufficient amount of ethanol, subsequently vacuum-dried, and then heated with a rotary tubular oven at 500° C. for 30 minutes in a nitrogen atmosphere to obtain a titania/silica-coated carbonyl iron powder B₆.

The thickness and refractive index of each layer of the thus-obtained multilayered film on the powder are shown in Table 1 below.

TABLE 1

Film Name	Film thickness (nm)	Refractive index
First layer, silica film	50	1.5
Second layer, titania film	37.5	2.0
Third layer, silica film	50	1.5
Fourth layer, titania film	37.5	2.0
Fifth layer, silica film	50	1.5
Sixth layer, titania film	37.5	2.0

Preparation of Colorant Composition and Spectral Characteristics

Two grams of this titania/silica-coated carbonyl iron powder B₆ was mixed with 10 g of a polyester resin varnish and 7 g of xylene as a solvent to prepare an ink. An A4 art paper was evenly coated with 5 g of the ink with a blade coater and then dried.

The coated paper obtained after drying had the spectral reflectance curve shown in FIG. 4. This coated paper was bright-blue, with a reflectance at 460 nm of 64%.

The coated paper reflected 93% of a light around 315 nm in the ultraviolet region and reflected 93% of a light around 1,115 nm in the infrared region. By detecting the two lights for discrimination, it is possible to judge genuineness by four means, i.e., magnetism, a visible light color, ultraviolet rays, and infrared rays.

Example 3

Process for Producing Purplish-red Multilayer-coated Powder

First Layer: Silica Coating

Into 100 ml of ethanol was dispersed 10 g of a magnetite powder (average particle diameter, 1.2 μm). Thereto were added 6 g of a silicon ethoxide, 8 g of 29% ammonia water, and 8 g of deionized water. The resultant mixture was reacted for 5 hours with stirring. After the reaction, the reaction mixture was diluted with ethanol and filtered. The particles were dried with a vacuum dryer at 110° C. for 8 hours. After the drying, the particles were heated with a rotary tubular oven at 650° C. for 30 minutes in a nitrogen atmosphere to obtain a silica-coated powder C₁. The film thickness of the silica-coated powder C₁ obtained was 75 nm. This powder was excellent in dispersed state. This silica-coated powder C₁ was heated.

Second Layer: Titania/silica Coating

To 10 g of the silica-coated powder C₁ obtained was added 200 ml of ethanol to disperse the particles. Thereto was added 3.5 g of titanium ethoxide. This mixture was stirred. A solution prepared by mixing 30 ml of ethanol with

3.5 g of water was added dropwise to the above mixture over 60 minutes, and the resultant mixture was reacted for 5 hours. Vacuum drying and heating were conducted in the same manners as for the first layer. Thus, a silica/titania-coated powder C₂ was obtained. The silica/titania-coated powder C₂ obtained had satisfactory dispersibility and was composed of independent particles.

The titania film of this silica/titania-coated powder C₂ had a thickness of 55 nm.

Third Layer: Silica Coating

Ten grams of the silica/titania-coated powder C₂ was dispersed into 100 ml of ethanol. Thereto were added 6 g of silicon ethoxide, 11 g of 29% ammonia water, and 8 g of water. The resultant mixture was reacted for 5 hours with stirring. After the reaction, the reaction mixture was diluted and washed with ethanol and filtered. The particles were dried for 8 hours in the same manner as for the first layer. After the drying, the particles were heated with a rotary tubular oven at 650° C. for 30 minutes to obtain a silica-coated powder C₃.

The film thickness of the silica-coated powder C₃ obtained was 78 nm. This powder was excellent in dispersed state.

Fourth Layer: Titania/silica Coating

To 10 g of the silica-coated powder C₃ obtained was added 200 ml of ethanol to disperse the particles. Thereto was added 3.8 g of titanium ethoxide. This mixture was stirred. A solution prepared by mixing 30 ml of ethanol with 3.8 g of water was added dropwise to the above mixture over 60 minutes, and the resultant mixture was reacted for 5 hours. Vacuum drying and heating were conducted in the same manners as for the first layer. Thus, a silica/titania-coated powder C₄ was obtained. The silica/titania-coated powder C₄ obtained had satisfactory dispersibility and was composed of independent particles.

This silica/titania-coated powder C₄ had satisfactory dispersibility and was composed of independent particles. The titania film as the fourth layer had a thickness of 57 nm.

Properties of the Coated Powder

The multilayer-coated powder thus obtained had reflection peaks at 380 nm and 780 nm with reflectances of 40% and 45%, respectively. It had a bright purplish-red color. This powder had a magnetization of 69 emu/g at 10 kOe.

Preparation of Heat-resistant Coating Material

To 50 parts by weight of a pure silicone resin was added 30 parts by weight of the purplish-red, multilayer-coated powder obtained above, followed by 50 parts by weight of benzene. The resultant mixture was kneaded and homogenized to obtain a coating composition.

The coating composition obtained was applied to an alumina ceramic plate. The composition applied was dried to obtain a coating film having a thickness of 12 μm. The coated plate was purplish-red. This coated plate was examined with a spectrophotometer to determine absorption wavelengths. As a result, the peak wavelength was 770 nm and the reflectance was 48%.

Furthermore, this coated plate was held in an oxygen atmosphere at 500° C. for 200 hours, subsequently cooled, and then examined with a spectrophotometer for absorption wavelengths. As a result, the peak wavelength was 768 nm and the reflectance was 49%, which were almost the same.

Industrial Applicability

According to the present invention, a colorant composition of a clear and stable color tone, such as, blue, green, yellow, or the like, can be obtained without using a dye or pigment.

Furthermore, since the composition has one or more interference reflection peaks also outside the visible light region, forgery prevention with an even higher degree of certainty is possible, besides visual recognition and magnetic printing, when the composition is used in combination with a reader for detecting reflected ultraviolet or infrared rays.

Moreover, powders having various properties, such as ferroelectric materials, conductive materials, and the like, can be utilizable. Even in the case of a magnetic material, it can be colored in a clear tint without impairing the magnetic properties.

In addition, by applying this colorant composition, a coating film is obtained which suffers neither discoloration nor color fading even at a high temperature of 350° C. to 600° C.

In particular, the powder used in the present invention comprises a base powder particle made of any of various materials suffering neither deformation nor discoloration at a high temperature of 350° C. to 600° C. and a light-interference multilayered film formed on the particle, and thus has a color different from that of the base powder particle and unchangeable thermally. Therefore, the powder gives a heat-resistant coating composition which suffers no color change at a high temperature and is capable of readily forming a heat-resistant coating film.

What is claimed is:

1. A colorant composition comprising at least a powder dispersed in a dispersion medium, said powder comprising a base particle coated with a multilayered film comprising layers differing from each other in refractive index and having a color due to light interference among the layers constituting the multilayered film, said powder having an interference reflection peak in the visible light region and an interference reflection peak outside the visible light region, wherein the thickness of each layer satisfies the following equation (1):

$$N \times d = m \times \lambda / 4 \quad (1)$$

wherein N represents a complex refractive index; d represents a basic film thickness; m represents an integer (natural number); λ represents a wavelength at which an interference reflection peak or interference transmission peak appears; and N is defined by the following equation (2):

$$N = n + ik \quad (2)$$

wherein n represents a refractive index of each unit coating layer; i represents a complex number; and k represents an extinction coefficient, the actual thicknesses of the unit coating layers being corrected to account for phase shift caused by the extinction coefficient k of the refractive index, the phase shift occurring at film interfaces, and the peak shift attributable to refractive index dispersion and particle shape so that the unit coating layers have interference reflection peaks or interference transmission bottoms at the same specific wavelength.

2. The colorant composition according to claim 1, wherein the base particle of the powder is a magnetic material.

3. The colorant composition according to claim 1, wherein the base particle of the powder is a dielectric material.

4. The colorant composition according to claim 1, wherein the base particle of the powder is a conductive material.

5. The colorant composition according to claim 1, wherein the base particle of the powder is made of a material

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which suffers neither deformation nor discoloration at a high temperature of 350° C. to 600° C.

6. The colorant composition according to claim 1, wherein at least one layer of the multilayered film of the powder is a metal compound layer.

7. The colorant composition according to claim 1, wherein at least one layer of the multilayered film of the powder is a metal layer or an alloy layer.

8. The colorant composition according to claim 1, wherein the dispersion medium comprises at least one resin and a solvent.

9. The colorant composition according to claim 8, wherein the resin is at least one heat-resistant resin.

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10. The colorant composition according to claim 9, wherein the heat-resistant resin is at least one selected from a pure silicone resin, a fluororesin, and a silicone-modified resin.

11. A color ink composition comprising the colorant composition according to claim 1.

12. A heat-resistant colorant composition comprising the colorant composition according to claim 1.

13. The colorant composition according to claim 1, wherein the powder is a spherical powder.

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US005763085A

United States Patent [19]

Atarashi et al.

[11] Patent Number: **5,763,085**[45] Date of Patent: **Jun. 9, 1998**

[54] **POWDER HAVING AT LEAST ONE LAYER AND PROCESS FOR PREPARING THE SAME**

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[21] Appl. No.: **532,994**

[22] Filed: **Sep. 25, 1995**

Related U.S. Application Data

[63] Continuation of Ser. No. 192,044, Feb. 4, 1994, abandoned.

[30] Foreign Application Priority Data

Feb. 5, 1993 [JP] Japan 5-040678
Sep. 16, 1993 [JP] Japan 5-252170

[51] Int. Cl.⁶ **B32B 5/16**

[52] U.S. Cl. **428/403; 428/570; 428/694 BA; 428/699; 428/701; 428/900**

[58] Field of Search **428/403, 570, 428/694 BA, 699, 701, 702, 900; 252/62.51, 62.55, 62.56**

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[57] ABSTRACT

A powder comprising a metal or metallic compound core having thereon at least one metal or metallic oxide layer having a uniform thickness of from 0.01 μm to 20 μm , wherein the metal of the metal or metallic oxide layer is different from the metal constituting the metal or metallic compound core and a process for preparing the same.

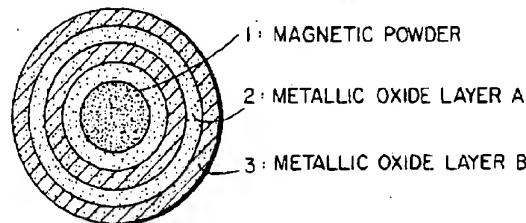
20 Claims, 1 Drawing Sheet

FIG. 1

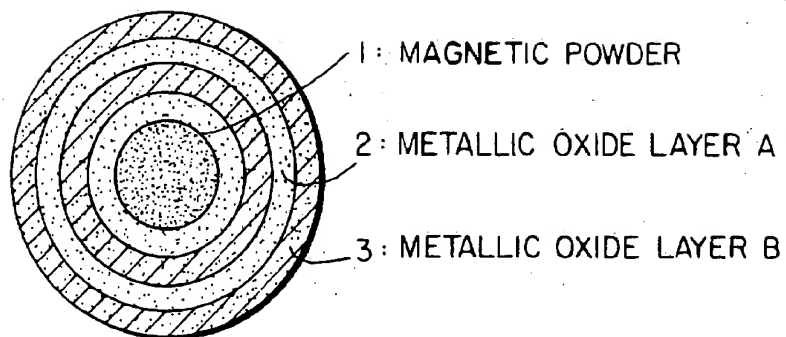
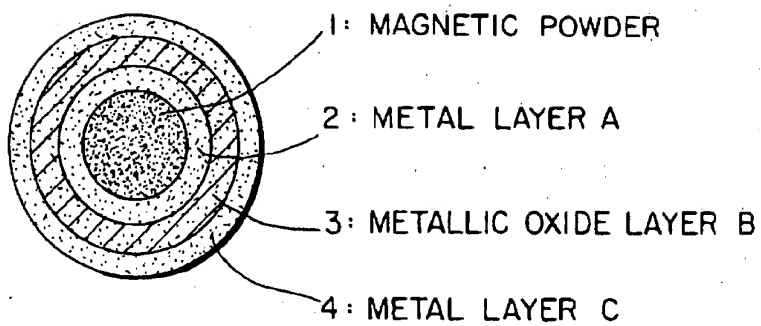


FIG. 2



POWDER HAVING AT LEAST ONE LAYER AND PROCESS FOR PREPARING THE SAME

This is a Continuation of application Ser. No. 08/192,044
filed Feb. 4, 1994 now abandoned.

FIELD OF THE INVENTION

This invention relates to a metal or metallic compound powder having on the surface thereof at least one thick metal or metallic oxide layer. More particularly, it relates to a novel metal or metallic compound powder composed of metal or metallic compound powder and a thick surface layer comprising an oxide of a different metal, in order to provide complex properties and to exhibit complex functions. More specifically, it relates to a magnetic powder or magnetic particle having multiple layers on the surface thereof which is useful as a starting material for color magnetic materials, such as color magnetic toners and color magnetic inks.

BACKGROUND OF THE INVENTION

It is well known that metallic materials or products, even with a polished finish, are covered with a thin oxide layer formed by oxidation in air. Known film formation techniques for protecting the surface of a product or for forming a thin film include coating, depositing, anodizing, sputtering, vacuum evaporation, electrodeposition, and so forth. Coating is suitable for obtaining a thick film, but the coating film is non-uniform in thickness and has poor adhesion. While anodizing, sputtering or vacuum evaporation provides a film having a fairly uniform composition with good adhesion, there is obtained only a thin film. Where anodizing is applied to an aluminum substrate, the resulting aluminum oxide layer is not dense. Electrodeposition and anodizing are not suitable for the treatment of powder because an object to be treated must serve as an electrode.

These conventional techniques can easily be carried out in cases where a substrate has a large size. However, they are not applicable to a powdered product without some additional techniques. Even when using additional techniques, it has been difficult to form a film of uniform thickness on the powder surface.

With reference to metal powder, formation of an oxide layer on the surface thereof is not difficult because the surface metal undergoes oxidation on exposure to an oxidizing atmosphere, thereby to form a thin oxide layer spontaneously. However, where the metal is very susceptible to oxidation or where the particle size is small, the spontaneous oxidation process cannot be adopted because the reaction proceeds too rapidly, leading to ignition. If the degree of oxidation is controlled, the resulting oxide layer would be too thin for practical use. While the surface of metal powder may be oxidized with an oxidizing agent in a liquid system, the contact with an oxidizing agent cannot be effected uniformly because of the heterogeneous system so that formation of a metallic oxide layer of uniform thickness has been difficult. If the reaction is controlled so as to form a dense oxide layer, it is difficult to form a thick film. Hence, it has not been easy to form a dense film to a desired film thickness.

It is more difficult to uniformly form an oxide layer of a metal different from the substrate metal powder. Although there is a technique of coating silicon oxide or titanium oxide on metal powder to a very small thickness for the purpose of surface treatment, the technique is accompanied

with difficulty in providing a uniform and large thickness. Where depositing and coating techniques, though capable of forming a thick film on a metallic substrate, are applied to metal powder, the metal powder must be kept in a dispersed state. As a result, particles formed solely of the coating substance are likely to be formed, in addition to the desired coated metal powder, only to provide a mixture of the powder of the coating substance and the coated metal powder. No technique is available for coating metal powder with an oxide of a different metal to a large thickness without producing particles solely comprising the metallic oxide.

Various difficulties are also met with in coating a powder of a metallic compound with an oxide of a metal different from that constituting the metallic compound. For example, in the case where a metallic compound is deposited on a powder in a metallic salt aqueous solution, and the deposit is heated to be converted to the corresponding oxide, the aqueous solution is impregnated into the substrate metallic compound. The result is that the deposited metallic compound, such as a metallic oxide, contains a different metallic oxide and that a dense oxide layer cannot be obtained.

It has been proposed to form a silver film on mica, which is a non-metallic object, by calcination and reduction for the purpose of imparting a metallic luster to mica as disclosed in JP-A-1-208324 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"). This process, however, involves a heat treatment in a high temperature and therefore cannot be applied to general powdered objects.

Further, KINZOKU HYOMEN GIJUTSU (*METAL SURFACE TECHNOLOGY*), Vol. 17, No. 8, p. 299 et seq. (1966) reports an electroless plating process for forming a metallic cobalt film on a plate, which comprises immersing a plate object in a cobalt complex salt aqueous solution and reducing the cobalt complex ion. However, these disclosures make no mention of formation of a plurality of layers.

With respect to formation of a metal coating layer on the surface of metal powder or metallic oxide powder, JP-A-3-271376 proposes a process for forming a metallic cobalt coating layer on the surface of a powdered metal, e.g., cobalt, nickel or iron, or a powdered metallic oxide, e.g., ferrite or chromium oxide, by reducing a water-soluble cobalt salt in a wet system. Similarly, JP-A-3-274278 discloses a process for forming a metallic silver coating layer on the surface of a powdered metal, e.g., cobalt, nickel or iron, or a powdered metallic oxide, e.g., ferrite or chromium oxide, by reducing a water-soluble silver salt in a wet system.

JP-A-60-184570 discloses a process for changing a color tone by forming a metallic oxide layer on a metallic oxide powder (mica). In this process, a titanium oxide is prepared by calcination after a titanium hydrate is formed on a surface of the powder in a solution of sulfate. This process, however, is not preferable because all metallic fine particles are dissolved when the particles are put into the solution according to this process.

With the recent advancement in various technological fields, there has been an increasing demand for metal or metallic compound powder having a specific function in addition to the properties essentially possessed by the powder.

For example, conventional magnetic powders, whose color is acceptable for use in conventional black magnetic toners, cannot be used as a material for color magnetic toners. Metal powder having high heat conductivity cannot

be used as such as a heat dissipating filler of a sealing compound for semiconductors, because it is required to have electrical insulating properties; metal powder for this use should have a surface layer with sufficient electrical insulating properties. Conventional methods for forming a thin oxide layer on the surface of a powder, which have been regarded as adequate for such purposes as protection of powder and facilitation of mixing of powder with a synthetic resin, etc., no longer meet these new demands. To satisfy these requirements, a powder having a novel structure is urgently required.

For the purpose of developing highly functional metal or metallic compound powders exhibiting specific properties in addition to the properties essentially possessed by the powder, the present inventors have made an effort to provide a metal or metallic oxide layer on the surface of metal or metallic compound powder as a core substrate.

However, it has been difficult to obtain a functional powder of good quality by forming a single coat on a powder substrate. For example, in preparation of white magnetic powder which can be used as a starting material for color magnetic materials, such as a color magnetic toner and a color magnetic ink, a coating layer comprising metallic cobalt or metallic silver may be formed on a powdered magnetic substance, such as metallic iron, ferrite or chromium oxide, according to the disclosure of JP-A-3-271376 or JP-A-3-274278. In this case, however, the coating layer should have a considerably large thickness, and even with a large thickness the resulting coated powder still has insufficient whiteness.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a metal or metallic compound powder having complex properties, suitable for performing complex functions to satisfy the new demands.

Another object of the present invention is to provide a metal or metallic compound powder with a metal or metallic oxide surface layer, and particularly a magnetic powder suitable as a material for preparing a color magnetic toner suited for use in an electrophotographic copying machine.

Still another object of the present invention is to provide a heat conductive powder having electrical insulating properties.

A further object of the present invention is to provide a process for preparing such a metal or metallic compound powder having complex properties and performing complex functions.

The present inventors have conducted extensive studies on various means for preparing powder satisfying the above-mentioned requirements. As a result, it has now been found that a thick and uniform metal or metallic oxide layer can be formed on a metal or metallic compound powder by dispersing the metal or metallic compound powder in a metal alkoxide solution and hydrolyzing the metal alkoxide.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1 and 2 each illustrates a cross section of a magnetic powder for color magnetic toners according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

More specifically, these and other objects of present invention are accomplished by (a) a powder comprising a

metal or metallic compound core having thereon a metal or metallic oxide layer having a uniform thickness of from 0.01 μm to 20 μm , wherein the metal of the metal or metallic oxide layer is different from the metal constituting the metal or metallic compound core; (b) a powder comprising a metal or metallic compound core having thereon at least two metal or metallic oxide layers each having a uniform thickness of from 0.01 μm to 20 μm , wherein the metal or metallic oxide layer which is in contact with the metal or metallic compound core is different from the metal constituting the metal or metallic compound core; (c) a process for preparing a powder comprising a metal or metallic compound core having thereon a metallic oxide layer by dispersing a metal or metallic compound powder in a solution of a metal alkoxide and hydrolyzing the metal alkoxide to form a metallic oxide layer on the surface of the metal or metallic compound powder; or (d) a process for preparing a powder comprising a metal or metallic compound core having thereon a metallic oxide layer and a metal layer by dispersing a metal or metallic compound powder, which may have a metal surface layer, in a solution of a metal alkoxide, hydrolyzing the metal alkoxide to form a metallic oxide layer on the surface of the metal or metallic compound powder, and forming a metal layer on the surface of the metallic oxide layer.

In particular, an excellent white magnetic powder or particle for use in production of color magnetic materials, such as color magnetic toners and color magnetic inks, can be obtained by forming a plurality of layers comprising at least one metal layer and at least one metallic oxide layer each having a uniform thickness of from 0.01 μm to 20 μm on the surface of a magnetic core metal or metallic compound.

For example, a metal layer is first formed on powder of a magnetic substance, e.g., metallic iron, ferrite or chromium oxide, a metallic oxide layer is then formed on the metal layer, and finally a coating layer of metallic cobalt or metallic silver is provided thereon.

Other types of powder having complex functions can also be obtained by formation of a metal layer and a metallic oxide layer on a powder substrate. For example, formation of a plurality of metal layers and metallic oxide layers on a metal powder substrate having satisfactory heat conductivity, such as metallic silver or metallic copper, provides powder having thereon an insulating layer with good adhesion, thereby exhibiting not only heat conductivity but insulating properties.

Further, in particular, an excellent white magnetic powder for use in production of color magnetic materials can be prepared by a process comprising dispersing a powder of a magnetic metal or metallic compound previously having thereon a metal layer in a solution of a metal alkoxide, hydrolyzing the metal alkoxide to form a metallic oxide layer on the surface of the metal layer of the metal or metallic compound, and forming a metal layer on the surface of the metallic oxide layer.

According to this process, by using a metal powder having a high reflectance as a substrate, an excellent white magnetic powder may be prepared even if the first step of forming the innermost metal layer is omitted, when the kind of metallic oxide layer, the kind of outermost metal layer, and the thickness of each layer are appropriately selected.

The term "at least two metal or metallic oxide layers" as used herein means (i) at least two metal layers, (ii) at least two metallic oxide layers, or (iii) at least one metal layer and at least one metallic oxide layer.

The term "metal" as used for metal and metallic compound (including metal powder and metallic compound powder) as used herein includes not only a metal, but also an alloy thereof. More specifically, the term "iron" includes iron alloys, e.g., iron-nickel and iron-cobalt; the term "iron nitride" includes an iron-nickel nitride and an iron-nickel-cobalt nitride; and the term "iron oxide" includes an iron-nickel oxide and an iron-nickel-cobalt oxide. Further, the term "metal alkoxide" includes mixed metal alkoxides. For example, a barium alkoxide may contain a calcium alkoxide. These examples are not to be construed as limiting the present invention, which includes other iron alloys, iron nitrides, iron oxides and metal alkoxides.

Formation of a metal layer on the surface of a powder substrate can be preferably carried out by electroless plating. It may be done by contact electroplating or sputtering as described in E. Takeshima, *FUNTAI KOGAKU KAISHI*, "The Approach to Creation of New Composite Materials", vol. 27 No. 7, pp. 480-484 (1990). However, in contact electroplating, plating would not be effected without contact of the powder with an electrode, and in sputtering, metal vapor is not uniformly applied to the powder. As a result, the thickness of the metal layer formed varies among individual particles. To the contrary, electroless plating provides a dense and uniform metal layer with easy control of thickness. The present invention will be explained chiefly referring to film formation by electroless plating, but the film formation technique employable in the present invention is not to be construed as being limited thereto.

The powdered metal, a substrate on which a metal or metallic oxide layer is to be formed, is not limited and includes iron, nickel, chromium, titanium and aluminum. The metal may be a magnetic metal. Magnetic metal powder, such as iron powder, is preferred for making use of its magnetic properties. As described above, the metal may be an alloy. Ferromagnetic alloys are preferred as magnetic powder.

In using a metal powder as a substrate, the process of the present invention typically includes first forming a metallic oxide layer on the substrate and then forming a metal layer thereon. If desired, a metallic oxide layer is further provided thereon. Where a metallic oxide layer is hard to adhere to the powdered metal, a metal layer may be provided on the substrate as a first step.

In using a metallic compound powder as a substrate, the process of the present invention typically includes first forming a metal layer on the substrate and then forming a metallic oxide layer thereon. The metal layer formation may further be followed by formation of a metallic oxide layer and then formation of a metallic oxide layer.

The metallic compound as a substrate typically includes a nitride of a metal or an alloy, a carbide of a metal or an alloy, and an oxide of a metal or an alloy. Examples of preferred metallic compounds are iron nitride, a nitride of an iron alloy, such as iron-nickel nitride or iron-cobalt nitride, and a metallic oxide, such as an oxide of iron, nickel, chromium, titanium, aluminum, silicon, calcium, magnesium or barium, and mixed compound oxides of these metals. These compounds may be magnetic or non-magnetic.

While not limiting, the particle size of the powder substrate is preferably from 0.01 μm to several millimeters, more preferably from 0.01 μm to 200 μm .

The metallic oxide which is to be formed on the surface of the substrate comprises a metal different from that constituting the substrate. Formation of a metallic oxide layer on powder of the same metallic oxide provides little technical benefit.

Examples of the metallic oxide include an oxide of iron, nickel, chromium, titanium, zinc, aluminum, cadmium, zirconium, silicon, calcium, magnesium or barium. The kind of the metallic oxide is selected appropriately according to the property to be imparted to the powder substrate.

Not only one but also a plurality of metal or metallic oxide layers may be provided. In either case, an individual layer has a thickness of from 0.01 μm to 20 μm , preferably from 0.02 μm to 5 μm . A plurality of metal or metallic oxide layers may be provided in such a manner that a layer of an oxide of a metal different from the metal of a powder substrate is first formed on the substrate and subsequently a metal or metallic oxide layer which may be either the same as or different from the first metal or metallic oxide layer is formed thereon. Where the substrate is a metallic oxide, it is recommended to form at least two metal or metallic oxide layers thereon.

A metal layer can be formed by dispersing a powder substrate in an aqueous solution of a complex salt of the metal and reducing the metal complex salt in the presence of the powder to form a layer of the metal on the surface of the powder.

Examples of the metal layer include a layer of silver, cobalt, gold, palladium, copper or platinum.

The above-mentioned metal complex salt is produced by adding a complexing agent to a water-soluble metal salt. For example, aqueous ammonia is added to silver nitrate, or an aqueous solution of sodium citrate or potassium tartrate is added to cobalt sulfate.

A metallic oxide layer can be formed by dispersing a powder substrate, i.e., metal powder, metallic compound powder or metal powder with a metal layer, in a solution of an alkoxide of a metal providing a desired metallic oxide, and hydrolyzing the metal alkoxide to form a corresponding metallic oxide on the powder substrate. The process utilizing hydrolysis of a metal alkoxide is called a sol-gel process, by which a fine oxide of uniform composition can be formed. Application of the sol-gel process to a powdered substrate provides a layer having a uniform and large thickness. A layer having a uniform thickness as used herein means a layer having a thickness of which fluctuation obtained from the observation of a cross section of the layer coated on the surface of the powder by SEM (Scanning Electron Microscope) is within 20%.

The metal alkoxide is selected according to the desired metallic oxide from among alkoxides of zinc, aluminum, cadmium, titanium, zirconium, tantalum, silicon, etc. In preparation of magnetic powder for magnetic toners, titanium oxide or silicon oxide is often used as a surface metallic oxide. In this case, a titanium alkoxide or a silicon alkoxide is chosen. Examples of the alkoxide include a monoalkoxide, such as methoxide, ethoxide, isopropoxide or butoxide, and a polymer of alkoxide, such as a polymer of isopropoxide or butoxide.

Since the metal alkoxide is decomposable with water, a metallic oxide should be used as a solution in an organic solvent. Suitable organic solvents include alcohols, e.g., ethanol and methanol, and ketones. It is preferable to use a dehydrated organic solvent. The concentration of the metal alkoxide is subject to variation depending on the kinds of the metal alkoxide and the organic solvent. The optimum concentration should be decided accordingly. The concentration of a metal alkoxide solution and the amount of the metal alkoxide solution based on the powder, determine the thickness of the metallic oxide layer to be formed on the powder. The concentration of the metal alkoxide solution depends on

the amount and particle size of the powder. For example, when a methoxide, an ethoxide, or an isopropoxide is used as the metal alkoxide, the concentration of the solution thereof is preferably from 0.1% to 80% because the metal alkoxide is hydrolyzed at a high rate. When a butoxide, a polymer of isopropoxide or a polymer of butoxide is used as the metal alkoxide, the concentration of the solution thereof is preferably from 0.1% to 90% though the metal alkoxide is hydrolyzed at a low rate. If the concentration of the solution exceeds the above upper limit, it is not preferable because oxide powders comprising the metal alkoxide which is to coat the metal or metallic oxide powder are produced as impurities. If the concentration of the solution is less than 0.1%, it is not preferable because the layer formed cannot function as an electrical insulating layer or a reflective layer in a visible ray region.

The metal or metallic compound powder is dispersed in the metal alkoxide solution, and water is added thereto to hydrolyze the metal alkoxide to produce a corresponding metallic oxide and, at the same time, to precipitate it on the powder to form a layer of the metallic oxide. The powder with the metallic oxide layer is taken out of the solution and dried to obtain powder having the metallic oxide layer with firm adhesion.

In carrying out the metallic oxide layer formation, the powder is dispersed, e.g., in a dehydrated alcohol, and a metal alkoxide solution is added thereto while thoroughly stirring. To the resultant uniform mixture is slowly added a mixture of alcohol and water to cause hydrolysis of the metal alkoxide thereby precipitating a metallic oxide on the surface of the powder. In the mixture of alcohol and water, the concentration of water is preferably from 0% to 60% of the total solution. If the concentration thereof exceeds 60%, it is not preferable because coarse powders consisting of a metal alkoxide are produced as impurities just after the mixture thereof is added dropwise. The metallic oxide layer thus formed on the powder is then dried to give coated powder. Drying is preferably conducted in vacuo.

The metallic oxide layer thus formed on the powder is then dried to give a powder with a single metallic oxide layer. In preparation of a powder with a plurality of metallic oxide layers, the above-described reaction step for metallic oxide layer formation is repeated as many times as desired, finally followed by drying.

In the hydrolysis system, a sol of a metallic oxide is first produced, which then sets to gel. After a while from completion of the hydrolysis, gelation proceeds. In some cases, gelation completes on drying. During the reaction, the sol is formed on the surface of the powder to provide a continuous film. Accordingly, a strong metallic oxide layer having a uniform thickness and a uniform composition can be formed easily. A metallic oxide layer having such properties cannot be obtained by any conventional film formation method, such as depositing.

If the hydrolysis system contains a large proportion of water, the reaction proceeds at a high rate so that fine metallic oxide particles are apt to be formed. In order to make the reaction milder, an amine may be added to the system. Examples of the amine include trimethylamine and diethylamine. The added amount thereof is preferably from 0% to 15% of the amount of the total solution. If desired, a catalyst, such as an acid, may be used for reaction acceleration. Examples of the acid include hydrochloric acid, acetic acid, nitric acid, oxalic acid, formic acid, and tartaric acid. The added amount thereof is preferably from 0% to 10% of the amount of the total solution. If the amount

exceeds 10%, it is not preferable because the oxide powders comprising the metal alkoxide are produced by the acceleration of the hydrolysis rate as impurities.

According to the process of the present invention, there is obtained a metallic oxide layer having excellent properties, unlike a metallic oxide layer simply resulting from surface oxidation of metal powder. The process is also useful in formation of a metallic oxide layer whose metal is the same as that constituting the powder substrate. Therefore, application of the process to preparation of metal or metallic compound powder having an oxide layer of the same metal as that of the powder is also included in the scope of the present invention.

The thus prepared metal or metallic compound powder having thereon a metallic oxide layer possesses various combined properties according to the material of the substrate and that of the surface metallic oxide, which may easily be selected to provide various useful properties for different purposes. For example, choice of magnetic powder, such as tri-iron tetroxide, as a substrate, silicon oxide having a lower refractive index than that of the substrate as a metallic oxide layer to be formed on the substrate, and metallic silver having a higher refractive index as a metal layer to be formed as an outer layer results in production of magnetic powder having a high degree of whiteness. When a metallic compound is used as a substrate, for example, silicon oxide having a lower refractive index than that of the substrate is coated as the first metallic oxide layer on the substrate; titanium oxide having a higher refractive index than that of the silicon oxide is coated as the second metallic oxide layer on the first layer; and metal having a lower refractive index is coated as an outer layer, since it is essential that the last layer has higher reflective index.

Further, choice of silver, copper or aluminum as a substrate; gold, platinum or silver as a metal layer to be formed on the substrate; and aluminum oxide as a metallic oxide layer to be formed thereon results in production of heat conductive powder with an electrically insulating surface layer.

When a transparent oxide dielectrics layer having a higher refractive index and a transparent oxide dielectrics layer having a lower refractive index are alternately laminated on the substrate (i.e., powder), and when the relationship among the layer thickness, the refractive index of dielectrics layer and the target wavelength satisfies the following equation (1), the oxide dielectrics reflective layer which reflects the vertical incident light of the target wavelength can be prepared:

$$nd=2m-\frac{1}{4}\lambda \quad (1)$$

wherein n represents a refractive index; d represents a layer thickness; λ represents a wavelength; and m represents an integer. nd , which represents the product of the refractive index and the actual layer thickness, is called as an optical layer thickness.

When light incidents on two layers of which refractive indexes are different, the light reflects on the boundary side thereof. When alternate layers each having a thickness corresponding to odd number times of a quarter of a wavelength, the light reflection becomes stronger and comes to be an interference reflection which produces a stationary wave having the wavelength. Accordingly, a white powder can be prepared by means that the powder has a plurality of layers each having an optical layer thickness corresponding to odd number times of a quarter of the wavelength, such as a quarter, three quarters, or five quarters of the wavelength.

More particularly, when a plurality of coating layers different in refractive index are each provided on the surface of an object to such a thickness that the product of the refractive index of the layer and the thickness of the layer corresponds to a quarter of the wavelength of electromagnetic waves, light is mostly reflected thereon by interference (Fresnel reflection). This phenomenon can be utilized to prepare magnetic powder for a magnetic toner which totally reflects light and shines in white. In greater detail, such a white magnetic powder can be prepared by selecting a powdered magnetic substance, such as metal (e.g., iron, cobalt or nickel), an alloy thereof or iron nitride, as a core material, forming thereon a metal layer having a high refractive index (e.g., silver or cobalt) to a thickness corresponding to a quarter wavelength of visible light, forming thereon a metallic oxide layer having a lower refractive index than that of a metal (e.g., silicon oxide or titanium oxide) to a thickness corresponding to a quarter wavelength of visible light, and further forming thereon a metal layer having a high refractive index (e.g., silver or cobalt) to a thickness corresponding to a quarter wavelength of visible light.

If a colored layer is provided on the resulting white magnetic powder, followed by formation of a resin layer thereon, a color magnetic toner can be produced. Because the wavelength of visible light has a range, the metal layers and metallic oxide layers alternating with each other may have somewhat different thicknesses within the range of a quarter of the visible light wavelength.

FIG. 1 illustrates a cross section of a particle having the above-mentioned structure, in which magnetic powder 1 as a core is provided with a plurality of metallic oxide layers A and a plurality of metallic oxide layers B.

FIG. 2 illustrates a cross section of a particle having the above-mentioned structure, in which magnetic powder 1 as a core is provided with a plurality of layers consisting of metal layer A, metallic oxide layer B, and outermost metal layer C.

Use of the aforesaid magnetic toner is well-known in the art in a conventional method such as now described, and is described in, for example, U.S. Pat. No. 3,909,258.

A photoreceptor is prepared by coating a conductive substrate, such as a polyester film having thereon a metal deposited layer, with a coating composition comprising a binder resin, such as an acrylic resin, being dispersed therein fine particles of a photoconductive semiconductor, such as zinc oxide, a sensitizing dye, a color sensitizer, a dispersant, etc. to form a photoconductive layer.

The photoreceptor is uniformly charged by corona discharge and exposed to light having reflected on an original copy to be copied whereupon a positive electrostatic latent image is formed on the photoreceptor. The latent image is transferred to a transfer material, such as paper, and a magnetic toner charged to polarity opposite to the positive latent image is adhered to the latent image by means of a magnetic brush comprising the magnetic toner. Removal of non-adhered toner particles from the transfer material gives a magnetic toner image corresponding to the original copy. The toner image is then fixed to obtain a copy. With white paper and a colored magnetic toner prepared by coloring the coated powder of the present invention, the resulting copy would be an image of outstanding quality. A colored magnetic toner can be prepared by means that a white magnetic toner is dyed with color organic dyes or pigments.

The present invention will now be illustrated in greater detail with reference to Examples, but the present invention is not to be construed as being limited thereto. Unless otherwise indicated, all parts, percents and ratios are by weight.

EXAMPLES

Example 1

Dehydrated Ethanol

General dehydrated ethanol was further dehydrated with Molecular Sieve 3A1/8 at least overnight, filtered in a gloved box purged with argon gas, and preserved in a glass bottle with a stopper. In what follows, "dehydrated ethanol" means the thus prepared one.

Slurry 1

A hundred grams of iron carbonyl powder (produced by BASF; average particle size: 1.8 μm) were put in a glass container equipped with a high-speed stirrer, and 300 ml of dehydrated ethanol was added thereto, followed by thoroughly stirring by means of the high-speed stirrer to prepare slurry 1.

Solution 1

In a gloved box purged with argon gas, 300 ml of dehydrated ethanol and 33 g of tetraethyl orthosilicate were measured or weighed and mixed in a glass bottle with a stopper to prepare solution 1. The glass bottle was sealed.

Slurry 2

The container containing solution 1 was taken out of the gloved box, and the content was poured into the container containing slurry 1 all at once. The mixture was thoroughly stirred at a high speed to prepare slurry 2.

Solution 2

To 200 ml of dehydrated ethanol was added 2.7 g of pure water to prepare solution 2.

Solution 2 was added dropwise to slurry 2 by means of a buret over 1 hour while stirring slurry 2 sufficiently that the powder therein did not sediment, to thereby conduct hydrolysis slowly. After the dropwise addition, the resulting slurry (slurry 3) was stirred for about 8 hours, followed by centrifugation. The supernatant liquor was discarded to collect solid matter 1. Solid matter 1 was dried in vacuo to obtain sample 1, which was silicon oxide-coated iron powder.

Sample 1 was found to have a silicon oxide (SiO_2) content of 6.3%, from which the thickness of the silicon oxide layer was found to be 0.18 μm .

The resulting silicon oxide-coated iron powder was poured into 300 ml of dehydrated ethanol, followed by thoroughly stirring to prepare a dispersion. To the dispersion was added a previously prepared mixed solution of 42 g of tetraethyl orthotitanate and 300 ml of dehydrated ethanol, and the stirring was continued to prepare slurry 4.

To slurry 4 while being stirred was added dropwise a previously prepared mixed solution of 3.3 g of pure water and 200 ml of dehydrated ethanol over 1 hour. After the addition, the stirring was continued for an additional period of 8 hours, followed by centrifugal separation. The precipitate thus collected was dried to obtain sample 2. Sample 2 had a titanium oxide (TiO_2) content of 11.1%, from which the thickness of the titanium oxide layer was found to be 0.16 μm .

Example 2

A hundred grams of iron nitride powder (produced by NITTETSU MINING CO., LTD.; average particle diameter: 0.8 μm) were thoroughly stirred in 300 ml of dehydrated ethanol in a high-speed stirring machine in the same manner as in Example 1 to prepare slurry 5. To slurry 5 was added a solution of 105 g of tetraethyl orthosilicate in 300 ml of

dehydrated ethanol, followed by mixing with stirring, and a solution of 8.6 g of pure water and 300 ml of dehydrated ethanol was further added thereto dropwise over 1 hour. After the addition, the stirring was continued for 10 hours, and the mixture was allowed to stand and separated into a solid and a liquid. The solid was dried in vacuo to obtain sample 3. Sample 3 contained 24.4% of silicon oxide, indicating that the thickness of the silicon oxide layer was 0.11 μm .

Sample 3 was dispersed in 300 ml of dehydrated ethanol to prepare slurry 6. To slurry 6 was dispersed a mixed solution of 300 ml of dehydrated ethanol and 163 g of tetraethyl orthotitanate, and a solution of 300 ml of dehydrated ethanol and 12.8 g of pure water was added thereto dropwise over 1 hour. After the addition, the mixture was stirred for 10 hours, allowed to stand, and separated into a solid and a liquid. The solid was dried in vacuo to obtain sample 4. Sample 4 contained 31.3% of titanium oxide, indicating that the thickness of the titanium oxide layer was 0.10 μm .

Example 3

In 300 ml of dehydrated ethanol was thoroughly stirred, 600 g of atomized copper powder (average particle diameter: 6.0 μm) in a high-speed stirring machine in the same manner as in Example 1 to prepare slurry 7. To slurry 7 was added a solution of 83 g of tetraethyl orthotitanate in 300 ml of dehydrated ethanol all at once, followed by thoroughly stirring at a high speed. A solution consisting of 6.5 g of pure water and 200 ml of dehydrated ethanol was further added thereto dropwise over 1 hour. After the addition, the stirring was continued for 8 hours, and the mixture was allowed to stand and separated into a solid and a liquid. The solid was dried in vacuo to obtain sample 5. Sample 5 had an average particle diameter of 6.4 μm and a titanium oxide content of 2.2%, from which the thickness of the titanium oxide layer was estimated at 0.3 μm .

Example 4

Formation of Metal Layer

A silver complex salt aqueous solution (hereinafter referred to as a silver liquid) and a solution of reducing agent (hereinafter referred to as a reducing liquid) were prepared as follows.

Silver Liquid Composition

Silver nitrate	3.75 g
Aqueous ammonia (sufficient amount for re-dissolving a precipitate formed)	
Water	65 ml
Sodium hydroxide	2.7 g/65 ml

In 30 ml of water was dissolved 3.75 g of silver nitrate. To the solution was added aqueous ammonia having a specific gravity of 0.88 whereupon black brown silver oxide was precipitated. Addition of more aqueous ammonia resulted in formation of a silver-ammonia complex, which was dissolved to form a silver liquid.

Reducing Liquid

Glucose	4.5 g
Tartaric acid	4 g
Dehydrated ethanol	100 ml
Water	1000 ml

Glucose and tartaric acid were successively dissolved in 1000 ml of water, and the solution was boiled for 10

minutes. After cooling to room temperature, dehydrated ethanol was added thereto to prepare a reducing liquid. Since the reducing power of the reducing liquid is highest after about 1 week from the preparation, it is recommended to prepare the reducing liquid beforehand.

To 130 ml of the silver liquid was added 75 g of iron carbonyl powder, followed by thoroughly stirring. To the resulting dispersion was added 130 ml of the reducing liquid, and the mixture was stirred.

The resulting metal-coated powder A was washed with distilled water, filtered, and dried at room temperature in vacuo for 8 hours. Metal-coated powder A had a total silver content of 2.3 g, from which the thickness of the formed metal layer was estimated at 0.015 μm .

Formation of Metallic oxide Layer

In 300 ml of dehydrated ethanol was dissolved 72 g of titanium ethoxide, and 75 g of metal-coated powder A was added thereto, followed by thoroughly stirring.

To the solution while being stirred was slowly added dropwise a previously prepared water-containing alcohol solution consisting of 36 g of distilled water and 300 g of ethanol. After the addition, the stirring was continued for an additional period of 5 hours, followed by filtration. The solid thus collected was dried at room temperature for 8 hours in a vacuum drier to obtain coated powder B. Coated powder B had a total titanium oxide (TiO_2) content of 25 g, from which the thickness of the titanium oxide layer was found to be 0.5 μm .

Formation of Metal Layer

A silver liquid and a reducing liquid were prepared in the same manner as described above, except that the silver liquid had the following composition.

Silver nitrate	4.75 g
Aqueous ammonia (sufficient amount for re-dissolving a precipitate formed)	
Water	83 ml
Sodium hydroxide	3.41 g/83 ml

To 166 ml of the silver liquid was added 75 g of coated powder B, followed by thoroughly stirring. To the resulting dispersion was added 166 ml of the reducing liquid, followed by stirring. In 5 minutes' stirring, silver began to precipitate and the precipitation completed in about 15 minutes. The thus obtained metal-coated powder C was washed with distilled water, filtered, and dried at room temperature in vacuo for 8 hours. Metal-coated powder C had a total silver content of 5.2 g, and subtraction of the formerly coated silver content gave 2.9 g, the silver content of the outermost metal layer, from which the thickness of the outermost layer was estimated at 0.015 μm .

Metal-coated powder C had a reflectance of 78% as measured with a whiteness meter. For comparison, the starting iron carbonyl powder had a reflectance of 21%, revealing a great increase in reflectance by formation of coating layers.

Comparative Example 1

Comparative Example 1 describes a powder where the thickness of the outermost layer is decreased.

Seventy-five grams of coated powder B prepared in the same manner as in Example 4 was dispersed in a previously prepared mixed solution of 30 ml of the same silver liquid as used in the treatment of coated powder B in Example 4 and 136 ml of water. To the dispersion was added 166 ml of the same reducing liquid as used in Example 4, and the mixture was allowed to stand for 1 hour for completion of silver precipitation.

The resulting coated powder had a total silver content of 2.8 g, indicating that the silver content of the outermost metal layer was 0.5 g, from which the thickness of the outermost layer was estimated at 0.003 μm .

The metal-coated powder assumed no white color as expected but a dark bluish gray color. This is considered to be because the outermost silver layer was so thin that light was absorbed and not reflected.

In addition, since the metal layers and metallic oxide layers according to the present invention have a uniform thickness and firm adhesion to the powder substrate, they constitute a useful multi-layered surface layer which does not separate the substrate.

Specific examples of the use of the powder according to the present invention include white magnetic powder for magnetic toners and heat conductive powder having electrical insulating properties. The latter is useful as a filler for sealing compounds for semiconductors or a heat dissipating sheet for insulation and heat dissipation of electronic parts.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. A white magnetic powder comprising a metal or metallic compound core having thereon at least two metal or metallic oxide layers each having a uniform thickness of from 0.01 μm to 20 μm , wherein the metal of the metal or metallic oxide layer which is in contact with the metal or metallic compound core is different from the metal constituting the metal or metallic compound core, and wherein said magnetic powder is white.

2. The white magnetic powder as claimed in claim 1, wherein the metal or metallic compound core is coated with a metallic oxide layer and the metallic oxide layer is coated with a metal layer.

3. The white magnetic powder as claimed in claim 2, which is further coated with at least one metal or metallic oxide layer having a uniform thickness of from 0.01 μm to 20 μm .

4. The white magnetic powder as claimed in claim 2, wherein the metallic oxide in the metallic oxide layer is selected from the group consisting of silicon oxide, iron oxide, nickel oxide, chromium oxide, titanium oxide, zinc oxide, aluminum oxide, cadmium oxide, zirconium oxide, calcium oxide, magnesium oxide and barium oxide.

5. The white magnetic powder as claimed in claim 1, wherein the metal or metallic compound core is coated with a metal layer, and the metal layer is coated with a metallic oxide layer.

6. The white magnetic powder as claimed in claim 5, which is further coated with at least one metal or metallic oxide layer having a uniform thickness of from 0.01 μm to 20 μm .

7. The white magnetic powder as claimed in claim 5, wherein the metallic oxide in the metallic oxide layer is selected from the group consisting of silicon oxide, iron oxide, nickel oxide, chromium oxide, titanium oxide, zinc oxide, aluminum oxide, cadmium oxide, zirconium oxide, calcium oxide, magnesium oxide and barium oxide.

8. The white magnetic powder as claimed in claim 7, wherein the metal or metallic compound core is coated with two metallic oxide layers.

9. The white magnetic powder as claimed in claim 8, which is further coated with at least one metal or metallic oxide layer having a uniform thickness of from 0.01 μm to 20 μm .

10. The white magnetic powder as claimed in claim 8, wherein the metallic oxide in each of the metallic oxide layers is selected from the group consisting of silicon oxide, iron oxide, nickel oxide, chromium oxide, titanium oxide, zinc oxide, aluminum oxide, cadmium oxide, zirconium oxide, calcium oxide, magnesium oxide and barium oxide.

11. The white magnetic powder as claimed in claim 1, wherein the metal or metallic compound core is coated with two metal layers.

12. The white magnetic powder as claimed in claim 11, which is further coated with at least one metal or metallic oxide layer having a uniform thickness of from 0.01 μm to 20 μm .

13. The white magnetic powder as claimed in claim 1, wherein the metals constituting adjacent metal or metallic oxide layers among the at least two metal or metallic oxide layers are different from each other.

14. The white magnetic powder as claimed in claim 1, wherein the metal or metallic compound in the metal or metallic compound core is selected from the group consisting of silicon oxide, iron oxide, nickel oxide, chromium oxide, titanium oxide, aluminum oxide, calcium oxide, magnesium oxide, barium oxide, and a mixed compound oxide thereof.

15. A white magnetic powder comprising a metal or metallic compound core having thereon (i) at least one metal or metallic oxide layer and (ii) at least one metallic oxide layer, each having a uniform thickness of from 0.01 μm to 20 μm , wherein the metal of the metal or metallic oxide layer which is in contact with the metal or metallic compound core is different from the metal constituting the metal or metallic compound core, and wherein said magnetic powder is white.

16. The white magnetic powder as claimed in claim 15, wherein the metals constituting adjacent metal or metallic oxide layers, among the (i) at least one metal or metallic oxide layer and (ii) the at least one metallic oxide layer, are different from each other.

17. The white magnetic powder as claimed in claim 15, which is further coated with at least one metal or metallic oxide layer having a uniform thickness of from 0.01 μm to 20 μm .

18. The white magnetic powder as claimed in claim 15, wherein the metal or metallic compound in the metal or metallic compound core is selected from the group consisting of silicon oxide, iron oxide, nickel oxide, chromium oxide, titanium oxide, aluminum oxide, calcium oxide, magnesium oxide, barium oxide, and a mixed compound oxide thereof.

19. The white magnetic powder as claimed in claim 15, wherein the metallic oxide in the metallic oxide layer or layers is selected from the group consisting of silicon oxide, iron oxide, nickel oxide, chromium oxide, titanium oxide, zinc oxide, aluminum oxide, cadmium oxide, zirconium oxide, calcium oxide, magnesium oxide and barium oxide.

20. A color magnetic material prepared by a process comprising the step of:

dyeing a white magnetic powder comprising a metal or metallic compound core having thereon at least two metal or metallic oxide layers each having a uniform thickness of from 0.01 to 20 μm , wherein the metal of the metal or metallic oxide layer which is in contact with the metal or metallic compound core is different from the metal constituting the metal or metallic compound core.

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US006207280B1

(12) **United States Patent**
Atarashi et al.

(10) Patent No.: **US 6,207,280 B1**
(45) Date of Patent: **Mar. 27, 2001**

(54) **MULTILAYER-COATED POWDER AND
PROCESS FOR PRODUCING THE SAME**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/202,212**

(22) PCT Filed: **Jun. 6, 1997**

(86) PCT No.: **PCT/JP97/01942**

§ 371 Date: **Mar. 29, 1999**

§ 102(e) Date: **Mar. 29, 1999**

(87) PCT Pub. No.: **WO97/47417**

PCT Pub. Date: **Dec. 18, 1997**

(30) **Foreign Application Priority Data**

Jun. 10, 1996 (JP) 8-147422

(51) Int. Cl.⁷ **B32B 5/16**

(52) U.S. Cl. **428/403; 427/212; 427/215; 428/404**

(58) Field of Search **428/403, 404; 427/212, 215**

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(57) **ABSTRACT**

In producing a multilayer-coated powder by coating the surface of a base powder of a metal, metal oxide, etc. with two or more layers of a metal oxide or the like, the films of a metal oxide or the like are formed through decomposition, etc. from a metal salt as an inexpensive material. This is attained by making the powder particles not to be attacked by acids, etc. when the metal salt decomposition or the like, which yields an acid, etc., is conducted. The multilayer-coated powder is characterized in that the multilayered film comprises at least one layer consisting of a metal hydroxide or metal oxide film formed by the hydrolysis of a metal alkoxide and, as a layer disposed on the outer side of that layer, a coating film consisting of a metal hydroxide or metal oxide film formed by a reaction, e.g., neutralization or pyrolysis, of a metal salt. Upon heating, the metal hydroxide or metal oxide film formed by the hydrolysis of a metal alkoxide becomes a dense metal oxide film.

6 Claims, 1 Drawing Sheet

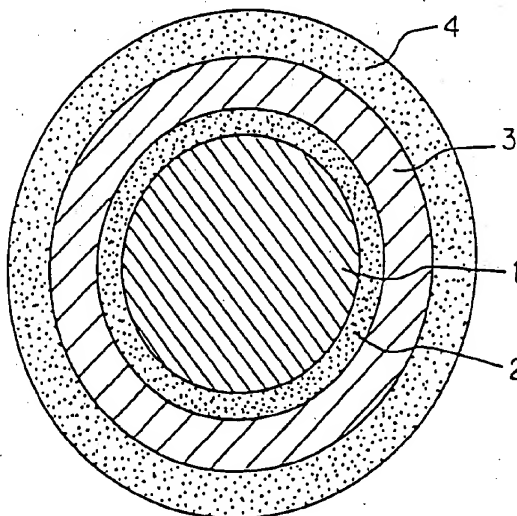
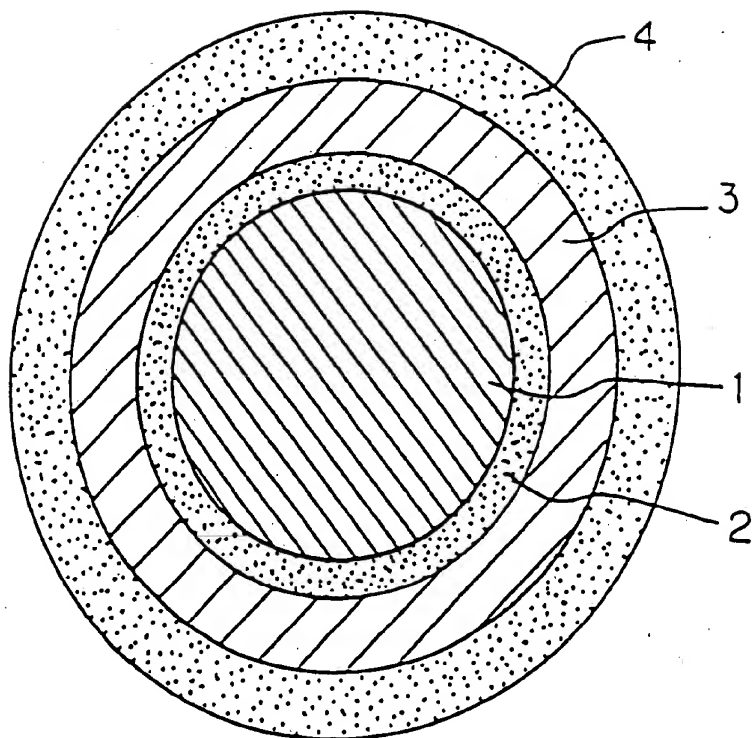


Fig. 1



MULTILAYER-COATED POWDER AND PROCESS FOR PRODUCING THE SAME

TECHNICAL FIELD

The present invention relates to a powder having a multilayered film on the surface and performing a combination of functions. More particularly, the present invention relates to a magnetic powder having a multilayered film on the surface and usable as a starting material for colored magnetic materials, such as magnetic color toners and magnetic color inks, and to a retroreflective pigment, a weather-resistant pigment, and the like.

BACKGROUND ART

Coating the surface of a powder with another substance has conventionally been conducted in order to obtain a powder having a special property or to modify the surface properties of the powder. Since it is difficult to evenly coat the surface of a powder having a small particle diameter, various methods have been investigated as powder-coating means.

Unexamined Published Japanese Patent Application No. 1-119062 discloses a technique for coating a powder with silver for the purpose of heightening the electroconductivity of the powder. Methods for forming a metal coating film on the surface of a metal or metal oxide powder are described, e.g., in Unexamined Published Japanese Patent Applications Nos. 3-271376 and 3-274278.

With respect to methods for forming a metal oxide coating film on the surface of a metal powder, a film of an oxide of the same metal can be obtained also by a method comprising placing the powder in an oxidizing atmosphere. However, this method is not applicable to the formation of a coating film of an oxide of another kind of metal. It is a matter of course that a completely different method should be used when the powder is made of a metal compound or a plastic.

A method usable for forming a coating film of a metal oxide on a powder comprises placing the powder in an aqueous solution of a metal salt, reacting the metal salt to cause precipitation and thus form a metal compound deposit layer on the powder particles, and drying or heating the covered particles to form a metal oxide layer to thereby obtain a coated powder. However, a dense oxide film is difficult to obtain by this method. If the above method is carried out so as to yield a dense oxide film, it is not easy to evenly form a dense film in a desired thickness, for example, because a large film thickness is difficult to obtain.

The present inventors previously invented a method for forming a film of a metal oxide by dispersing a metal powder or a metal oxide powder into a metal alkoxide solution and hydrolyzing the metal alkoxide, and made an application for patent (Unexamined Published Japanese Patent Application No. 6-228604).

The present inventors further developed highly functional powders by alternately forming a metal film and a metal oxide film on the surface of a metal powder or a metal oxide powder, and made an application for patent (Unexamined Published Japanese Patent Application No. 7-90310). For example, the inventor succeeded in obtaining a magnetic powder of a sufficiently white color by forming a coating film of a metal oxide on the surface of a magnetic material powder, such as ferrite or chromium oxide, and forming a coating film of cobalt metal or silver metal thereon, and also in obtaining an insulating powder having satisfactory thermal conductivity by forming a metal oxide film on a powder

of a metal having satisfactory thermal conductivity, such as silver metal or copper metal. Furthermore, the present inventors made an application for patent concerning a process which comprises similarly forming a multilayered metal oxide film on the surface of a metal powder or metal compound powder and heating the powder coated with the multilayered metal oxide film to produce a powder having a multilayered denser and more stable metal oxide film (WO96/28269).

As described above, the present inventors have made efforts with a view to developing a highly functional metal or metal compound powder by forming one or more films of a metal oxide or metal on the surface of a metal powder or metal compound powder to thereby impart a property other than those possessed by the metal or metal compound powder serving as core particles.

However, the above-described method in which a metal alkoxide is used as a starting material for forming a film of a metal oxide on the surface of a metal powder or metal compound powder has a drawback that the product developed with the alkoxide has very limited uses because the metal alkoxide is an expensive compound and, hence, the product is, of course, costly.

Although the method in which a film of a metal oxide is formed by precipitation from an aqueous metal salt solution has the problem that an even metal oxide film is difficult to obtain, it has a more serious drawback. Namely, since an acid or alkali is used in reacting the aqueous metal salt solution to cause precipitation or since the reaction yields an acid or alkali as a by-product, the powder particles serving as cores are attacked by the acid or alkali used as a reactant or yielded as a by-product and are thus dissolved, especially when the particles are made of a metal. Because of this drawback, the above method cannot be applied.

An object of the present invention is to eliminate the drawbacks of the above-described prior art techniques and to provide: a highly functional metal or metal compound powder inexpensively; and a technique with which a metal film or a metal oxide film can be formed on an organic powder or the like, and which is applicable to a wide range of powders besides metal or metal compound powders, e.g., organic powders.

DISCLOSURE OF THE INVENTION

The present inventors made investigations on whether or not the deposition method based on precipitation from an aqueous metal salt solution, which method is a conventional means for easily and inexpensively forming a metal oxide film, is applicable. As a result, it has been found that when base particles coated with a metal oxide film formed by the hydrolysis of a metal alkoxide are subjected to the deposition method based on precipitation from an aqueous metal salt solution, the base particles are protected by the metal oxide film formed by the hydrolysis of a metal alkoxide and are hence never attacked even when the precipitation reaction is conducted under such conditions that the base particles are attacked, because the metal oxide film is exceedingly dense as stated above. The present invention has been achieved based on this finding.

Specifically, the various problems described above have been eliminated by the following multilayer-coated powder and process for producing the same according to the present invention:

(1) A multilayer-coated powder, wherein at least one layer of the multilayer comprises a metal hydroxide film or a metal oxide film formed by hydrolysis of a metal alkoxide

having thereon a coating film comprising a metal hydroxide film or a metal oxide film formed by a reaction of a metal salt in an aqueous solution;

- (2) The multilayer-coated powder according to the above (1), wherein the metal hydroxide or the metal oxide film formed by the hydrolysis of a metal alkoxide is heated;
- (3) The multilayer-coated powder according to the above (1) or (2), wherein the metal hydroxide or the metal oxide film formed by the reaction of a metal salt in an aqueous solution is heated after the formation;
- (4) A process for producing a multilayer-coated powder, which comprises: forming a metal hydroxide film or a metal oxide film as at least one layer of a multilayered film by hydrolysis of a metal alkoxide; and forming thereon a coating film of a metal hydroxide film or a metal oxide film by a reaction of a metal salt in an aqueous solution;
- (5) The process for producing a multilayer-coated powder according to the above (4), wherein the metal hydroxide film or the metal oxide film is formed by the hydrolysis of a metal alkoxide, and then heated;
- (6) The process for producing a multilayer-coated powder according to the above (4) or (5), wherein the metal hydroxide film or the metal oxide film is formed by the reaction of a metal salt in an aqueous solution, and then heated.

In the present invention, the powder serving as the base of the multilayer-coated powder of the present invention can be a powder made of an organic substance as well as a powder made of an inorganic substance. Examples of the inorganic substance constituting the inorganic powder in the present invention include metals, such as, iron, nickel, chromium, titanium, and aluminum; metal alloys, such as iron-nickel and iron-cobalt alloys; iron-nickel alloy nitrides; iron-nickel-cobalt alloy nitrides; metal oxides, such as oxides of, e.g., iron, nickel, chromium, titanium, aluminum, and silicon (in this case, silicon is classified in metals); oxides of alkaline earth metals, such as calcium, magnesium, and barium; composite oxides of these, clays, and glasses.

Since one object of the present invention resides in the production of a powder having magnetic properties, such as a magnetic color toner or a magnetic color ink; it is preferred in this case to use a ferromagnetic substance as the base powder of the multilayer-coated powder of the present invention. The ferromagnetic substance may be a metal having a high magnetic permeability, such as iron, nickel, chromium, titanium, or aluminum. However, a ferromagnetic oxide or alloy can also be used, such as ferrite or γ -iron oxide.

Also usable as the base powder material in the present invention is a powder made of an organic substance. Examples of the organic substance constituting the base powder in the present invention include natural and synthetic polymers. Examples of the synthetic polymers include polystyrene, polyethylene, polypropylene, polyacrylic esters, polymethacrylic esters, and copolymers of any of the monomers of these polymers with one or more other monomers. Examples of the natural polymers include starch, agarose, cellulose, and gelatin. Other usable examples include semisynthetic polymers, such as acetyl cellulose and hydroxyethyl cellulose. Although the powder of an organic polymer may have irregular particle shapes, it is preferably composed of spherical particles formed by the suspension polymerization method or seed polymerization method or formed by the solution dispersion method or the like. Although some of those organic substances, when in direct contact with an aqueous metal salt solution, may suffer

surface corrosion depending on conditions for the reaction of the solution, this influence can be prevented by the present invention.

If a substance which withstands dilute strong acids, such as ferrite, γ -iron oxide, or titanium oxide, is used as a core material, the core particles hardly suffer surface corrosion even when exposed directly to a reaction of an aqueous metal salt solution. However, since the solution may have entered inner parts of the particles, there is a possibility that the multilayer-coated powder produced using the core particles might have been denatured.

Powders, such as an iron metal powder, nickel metal powder, aluminum metal powder, polystyrene beads, polymethacrylic ester beads, starch beads, and acetyl cellulose beads, suffer surface denaturation in an aqueous solution of a strong acid even when the acid concentration is low, and this may influence the quality of the final product, for example, by causing devitrification. Consequently, if such a substance is used as a core material, it is undesirable to use a metal salt, such as titanium sulfate, titanium chloride, or aluminum sulfate, as a material for forming a metal oxide coating film on the surface of the core material.

With respect to metal salts for use in the treatment based on precipitation by a reaction of an aqueous metal salt solution, which is the most common reaction among reactions of the above-described metal salts, the above problems are severer especially when an acid salt of a metal is used. Although neutralization or pyrolysis is typically used among reactions of a metal salt in an aqueous solution, other reactions may be used.

Examples of the metal used as a metal salt in the present invention include iron, nickel, chromium, titanium, zinc, aluminum, cadmium, zirconium, silicon, tin, lead, lithium, indium, neodymium, bismuth, cerium, antimony, calcium, magnesium, and barium. Examples of salts of these metals include salts of sulfuric acid, nitric acid, hydrochloric acid, oxalic acid, carbonic acid, and carboxylic acids. Chelate complexes of the above metals are also included. A suitable kind of metal salt for use in the present invention is selected according to the property to be imparted to the surface of the powder and the means to be used for production.

In the present invention, a film of a metal oxide or metal hydroxide is first formed by the hydrolysis of a metal alkoxide on particles serving as the base of a multilayer-coated powder, in order to protect the particles. If a metal film is to be formed as one of the layers of the multilayer-coated powder, this metal film should be formed under the metal oxide or metal hydroxide film formed from a metal alkoxide. Accordingly, a metal film may be formed directly on the surface of the base particles. If plural layers of a metal oxide or metal hydroxide film are formed from a metal alkoxide, a metal film can be formed between these layers. It is, however, undesirable to form a metal film over the metal oxide or metal hydroxide films.

In the present invention, an alkoxide of the same metal as that contained in the metal hydroxide or metal oxide film to be deposited as a coating film on the surface of particles serving as the base of a multilayer-coated powder is hydrolyzed to form a film of the metal hydroxide or metal oxide.

This method comprises dispersing the powder serving as a base material into a solution of the metal alkoxide (mostly in an organic solvent or in a mixed solvent consisting of an organic solvent and water) and adding water or a weakly alkaline aqueous solution to the solution containing the dispersed particles to hydrolyze the metal alkoxide and thereby form a film of a hydroxide or oxide of the metal on the surface of the particles.

Processes for producing a powder having a multilayered metal oxide film using the above method are described in Unexamined Published Japanese Patent Applications Nos. 6-228604 and 7-90310.

The above method for forming a metal oxide by hydrolysis is called a sol-gel method, and is effective in forming an oxide having a fine and homogeneous composition. By applying this method to a powder, a film which is even, thick, and dense is obtained on the powder particles. As the metal alkoxide is selected an alkoxide of the metal corresponding to the desired metal oxide, such as zinc, aluminum, cadmium, titanium, zirconium, tantalum, or silicon.

A metal alkoxide decomposable with water is generally used as a solution in an organic solvent. Usable organic solvents include, for example, alcohols, such as ethanol and methanol, and ketones. It is preferred to use a dehydrated organic solvent. Although the concentration of the metal alkoxide solution varies depending on the kind of the metal alkoxide to be dissolved and on the kind of the organic solvent, optimum conditions are used. The thickness of the metal hydroxide or metal oxide film formed on a powder is determined by the concentration of the metal alkoxide solution and the use amount of the metal alkoxide solution relative to the powder amount.

The powder on which a metal oxide film has deposited is taken out of the solution and dried, whereby a strong metal oxide film is obtained. The drying is preferably conducted in vacuo. If an inorganic powder was used as base particles, it is preferred to further conduct a heat treatment in vacuo or in an inert atmosphere at 200 to 800° C for 0.5 to 6 hours, because this treatment makes the film stronger.

As stated, a metal hydroxide film or metal oxide film is deposited by a reaction of a metal salt in an aqueous solution on the powder particles on the surface of which a metal hydroxide or metal oxide film has been formed from a metal alkoxide.

One method for accomplishing the above uses a metal salt, such as titanium sulfate or aluminum sulfate, as a starting material, and comprises immersing the base particles in an aqueous solution of the metal salt and neutralizing the system with an aqueous solution of a caustic alkali, ammonia, urea, or the like to thereby deposit the resultant metal hydroxide or metal oxide on the powder particles.

Another method for depositing a metal oxide film on the surface of powder particles in the present invention uses a metal salt, such as titanium sulfate or zirconium sulfate, which upon heating decomposes to deposit titanium oxide or zirconium oxide. This method comprises immersing the powder particles in an aqueous solution of such a metal salt and decomposing the metal salt by heating to deposit a metal oxide film on the powder particles and thus form a coating film.

Plural layers of a metal oxide film or the like may be formed from such a metal salt. It is also possible, if desired, to form a film of a metal oxide or the like from a metal alkoxide on these films of a metal oxide or the like.

Thus, a multilayered film can be formed on the powder particles serving as a base. In forming the film, desired properties can be obtained by using such film-forming conditions that each layer has a given thickness.

The particles thus obtained according to the present invention by forming a film of a metal oxide or the like from a metal alkoxide on the surface of base powder particles are not adversely influenced by the treatment for forming thereon a film of a metal oxide or the like from a metal salt. Consequently, a multilayered film of a metal oxide or the like can be formed by a simple procedure using a metal salt

as an inexpensive starting material. In particular, that a multilayer-coated powder can be obtained without using an expensive metal alkoxide as a starting material is an important advantage.

In processes for producing the multilayer-coated powder of the present invention, a multilayered film can be formed in various methods. For example, a multilayered film may be formed through continuous steps, or individual coating films may be formed one by one. Alternatively, the formation of a single layer and the continuous formation of plural layers may be conducted in combination.

For the coating with a metal film, contact electroplating or sputtering may be used, besides electroless plating. However, in the contact electroplating, powder particles not in contact with an electrode cannot be plated. In the sputtering, a metal vapor cannot be evenly applied to the powder particles. Hence, the thickness of the coating formed by either method varies from particle to particle. In contrast, the method of film formation by electroless plating is preferred in that a dense and even film can be formed and the film thickness is easy to regulate.

Since the thus-produced powder having a multilayered metal oxide film on the surface can have various properties imparted thereto according to the material of the powder selected and the material of the metal oxide constituting the surface coating film, it can be used in applications for respective purposes. For example, when a magnetic material, such as iron metal, iron nitride, or tri-iron tetroxide, is used as a powder and this powder is coated with silicon oxide, having a lower refractive index than the magnetic material, and further with a layer of titanium oxide, having a higher refractive index, as an outer film, then a magnetic powder having a high degree of whiteness is obtained. When a conductor, such as silver, copper, or aluminum, is used as a powder base and this metal layer is coated with a film of an electrically insulating metal oxide, such as aluminum oxide, then a thermally conductive powder having an electrically insulating surface layer is obtained.

Furthermore, when, for example, coatings having different refractive indexes are formed on a surface of an object each in such a thickness that the product of the refractive index of the substance constituting the film and the thickness of the film corresponds to one-fourth the wavelength of an electromagnetic wave, then most of the light is reflected due to interference (Fresnel reflection). This function can be utilized to produce a magnetic powder for magnetic toners which reflects light and has a shining white color by using a magnetic material, such as a powder of a metal, e.g., iron, cobalt, or nickel, an alloy powder, or an iron nitride powder as cores, forming a layer of a high-reflectance metal, such as silver or cobalt, on the surface of the cores, further forming on the outer side thereof a layer of an oxide having a lower refractive index than that metal, such as silicon oxide, in such a thickness that the product of the refractive index of the oxide and the thickness of this film is one-fourth a wavelength of visible light, and then coating this film with a layer of a high-refractive-index oxide, such as zirconium oxide, in such a thickness that the product of the refractive index of the material and the thickness of this film is one-fourth a wavelength of visible light.

The powder produced may be heated in an inert gas atmosphere at a temperature of from 200 to 800° C. Thus, a stronger powder having a higher degree of whiteness is obtained. If the above heat treatment of the powder is conducted, the powder obtained through the heat treatment should satisfy the requirement that in each layer the product

of the refractive index of the material and the film thickness is one-fourth a wavelength of visible light.

Forming a colored layer on this powder and further forming a resin layer thereon gives a magnetic color toner. Since visible light has wavelengths distributed in a certain width, each of the particles constituting the magnetic toner may have oxide layers formed alternately with metal layers so that these layers have slightly different thicknesses within a range in which the product of the refractive index of the material and the film thickness is close to one-fourth a wavelength of visible light.

In producing a multilayer-coated powder as a powder colored by interference reflection, a high-refractive-index film and a low-refractive-index film are alternately formed in respective thicknesses necessary for Fresnel interference so that light of target spectral wavelengths is reflected.

FIG. 1 illustrates a powder particle by means of a sectional view. This sectional view shows a powder particle colored by interference reflection, which comprises a particle 1 (glass bead) as a base, a metal film 2 formed on the surface thereof, a low-refractive-index metal oxide film A indicated by 3 formed on the film 2 from an alkoxide, and a high-refractive-index metal oxide film B indicated by 4 formed on the film A.

Starting materials, especially metal salts, used in the present invention will be explained below.

Preferred materials used for forming high-refractive-index films include: titanium compounds, such as halides and sulfate for titanium oxide films; zirconium compounds, such as halides, sulfate, carboxylates, oxalate, and chelate complexes for zirconium oxide films; cerium compounds, such as halides, sulfate, carboxylates, and oxalate for cerium oxide films; bismuth compounds, such as halides, nitrate, and carboxylates for bismuth oxide films; and indium compounds, such as halides and sulfate for indium oxide films.

Preferred materials used for forming low-refractive-index films include: sodium silicate, water glass, silicon halides, organosilicon compounds such as alkyl silicates, and polymers thereof for silicon oxide films; aluminum compounds, such as halides, sulfate, and chelate complexes for aluminum oxide films; and magnesium compounds, such as sulfate and halides for magnesium oxide films.

In the case of forming a titanium oxide film, for example, use of a mixture of titanium chloride and titanium sulfate is effective, for example, in giving a film of rutile titanium oxide, having a high refractive index, at a lower temperature.

The reaction for each coating is conducted while regulating the reaction temperature so as to be suitable for the kind of the metal salt or metal alkoxide, whereby a more perfect oxide film can be formed.

After a coating film has been formed, a heat treatment is preferably conducted to completely convert the film into an oxide film.

If hydroxide films or oxide films formed are heated, the heating may be conducted for every coating layer. Alternatively, the heat treatment may be conducted as the final step after the desired multilayered film has been completed.

If a magnesia film has been formed, this film is preferably coated with a titanium alkoxide in an organic solvent, preferably an alcohol, because magnesia is susceptible to hydration.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a sectional view of one embodiment of the multilayer-coated powder according to the present inven-

tion. This embodiment comprises particle 1 as a base, metal layer 2 formed on the surface thereof, and formed thereon low-refractive-index metal oxide film 3 and high-refractive-index metal oxide film 4.

BEST MODES FOR CARRYING OUT THE INVENTION

Processes for producing multilayer-coated powders each having plural metal oxide films on the surface, will be explained below by reference to Examples. However, the present invention should not be construed as being limited by the following Examples.

EXAMPLE 1

Formation of Metal Oxide Films: (coating of the surface of iron metal powder with titania film and silica film):

First Layer: Silica Coating:

To 20 g of a spherical iron metal powder (average particle diameter, 1.8 μm) was added 100 ml of ethanol to disperse the powder. The container was heated in an oil bath to keep the temperature of the liquid at 55° C. Thereinto were added 6 g of silicon ethoxide, 6 g of ammonia water (29%), and 8 g of water. This mixture was allowed to react for 3 hours under stirring. After the reaction, the reaction mixture was diluted and washed with a sufficient amount of ethanol and filtered. The solid matter was dried in a vacuum dryer at 180° C for 8 hours. After the drying, the resultant powder was heated with a rotary tubular oven in a nitrogen atmosphere at 650° C for 30 minutes to obtain silica-coated powder A. The silica-coated powder A obtained was excellent in dispersed state.

Second Layer: Titania Coating:

Into a solution prepared by dissolving 16 g of titanyl sulfate in distilled water was dispersed 10 g of the silica-coated powder A obtained above. The container containing the dispersion was heated in an oil bath to hold the dispersion at 90° C for 6 hours.

After the holding, the reaction mixture was washed with a sufficient amount of distilled water until the pH thereof became 5, and the powder was then dried for 8 hours. After the drying, titania-silica-coated powder A was obtained. The titania-silica-coated powder A obtained had satisfactory dispersibility and was composed of independent particles.

This powder had a spectral reflection curve having a peak wavelength of 558 nm and had a reflectance at the peak wavelength of 33%. It was blue-green.

COMPARATIVE EXAMPLE 1

Formation of Metal Oxide Film: (titania coating of the surface of iron metal powder without silica coating):

A container containing 100 ml of deionized water was heated in an oil bath to hold the deionized water at 80° C. Into this heated deionized water was dispersed 10 g of carbonyl iron powder A. A solution prepared by dissolving 7 g of titanium tetrachloride in 100 ml of ethanol was added dropwise over 60 minutes to the dispersion under stirring.

After the dropwise addition, a decomposition reaction for film formation was conducted for 2 hours while maintaining the temperature at 80° C.

At the time when the reaction was completed, the solid matter had turned into a yellow powder and the iron powder had completely dissolved away, leaving the titania gel only.

It is thought that the iron powder was dissolved in the presence of the titanium tetrachloride or by the hydrochloric acid which generated during titania formation from the chloride. Consequently, the formation of a titania film is impossible if an oxide film has not been formed beforehand.

EXAMPLE 2

Formation of Metal Oxide Films: (coating of the surface of iron metal powder with titania film and silica film): First Layer: Silica Coating:

Silica coating was conducted in the same manner as in Example 1. To 20 g of a spherical iron metal powder (average particle diameter, 1.8 μm) was added 100 ml of ethanol to disperse the powder. The container was heated in an oil bath to keep the temperature of the liquid at 55° C. Thereto were added 6 g of silicon ethoxide, 6 g of ammonia water (29%), and 8 g of water. This mixture was allowed to react for 3 hours under stirring. After the reaction, the reaction mixture was diluted and washed with a sufficient amount of ethanol and filtered. The solid matter was dried in a vacuum dryer at 180° C for 8 hours. After the drying, the resultant powder was heated with a rotary tubular oven in a nitrogen atmosphere at 650° C for 30 minutes to obtain silica-coated powder B. The silica-coated powder B obtained was excellent in dispersed state.

Second Layer: Titania Coating:

A container containing 100 ml of deionized water was heated in an oil bath while keeping the oil temperature at 80° C. Into the heated deionized water was dispersed 10 g of the silica-coated powder B. A solution prepared by dissolving 7 g of titanium tetrachloride in 100 ml of ethanol was added dropwise over 60 minutes to the dispersion under stirring.

After the dropwise addition, a decomposition reaction for film formation was conducted for 2 hours while maintaining the temperature at 80° C.

After completion of the reaction, the solid matter was taken out by filtration and washed with a sufficient amount of distilled water and finally with ammonia water to adjust the pH to 8. Thereafter, 200 ml of ethanol was added to wash the solid matter, which was then dried in a vacuum dryer.

The titania-silica-coated powder B obtained had a spectral reflection curve having a peak wavelength of 660 nm, with a reflectance of 40%. It was a skin-colored powder.

EXAMPLE 3

First Layer: Silica Coating:

To 20 g of a spherical iron metal powder (average particle diameter, 1.8 μm) was added 100 ml of ethanol to disperse the powder. Thereto were added 6 g of silicon ethoxide, 11 g of ammonia water (29%), and 8 g of water. This mixture was allowed to react for 3 hours under stirring. After the reaction, the reaction mixture was diluted and washed with a sufficient amount of ethanol and filtered. The solid matter was dried in a vacuum dryer at 180° C for 8 hours. After the drying, the resultant powder was heated with a rotary tubular oven in a nitrogen atmosphere at 650° C for 30 minutes to obtain silica-coated powder C. The silica-coated powder C obtained was excellent in dispersed state.

Second Layer: Titania Coating:

A container was heated in an oil bath while keeping the oil temperature at 80° C. Into 100 ml of heated deionized water was dispersed 10 g of the silica-coated powder C. A solution prepared by mixing 100 ml of ethanol with 11 g of titanium tetrachloride was added dropwise over 60 minutes to the dispersion under stirring.

After the dropwise addition, a decomposition reaction for film formation was conducted for 2 hours while maintaining the temperature at 80° C.

After completion of the reaction, the solid matter was taken out by filtration and washed with a sufficient amount of distilled water and finally with ammonia water to adjust the pH to 8. Thereafter, 200 ml of ethanol was added to wash the solid matter, which was then dried in a vacuum dryer. After the drying, the resultant powder was heated with a

rotary tubular oven in a nitrogen atmosphere at 650° C for 30 minutes to obtain titania-silica-coated powder D.

The titania-silica-coated powder D obtained was excellent in dispersed state. It was a skin-colored powder which had a spectral reflection curve having a peak wavelength of 660 nm, with a reflectance of 40%.

Third Layer: Silica Coating:

To 20 g of the titania-silica-coated powder D was added 100 ml of water to disperse the powder. Thereto were added 11 g of water glass and 8 g of water. Furthermore, 250 ml of 0.05 mol/l aqueous hydrochloric acid solution was added dropwise over 1 hour to the above mixture under stirring. The resultant mixture was heated to 80° C and allowed to react for 3 hours.

After completion of the reaction, the reaction mixture was diluted and washed with a sufficient amount of distilled water and filtered. The solid matter was dried in a vacuum dryer at 180° C for 8 hours. After the drying, the resultant powder was heated with a rotary tubular oven in a nitrogen atmosphere at 650° C for 30 minutes to obtain silica-titania-silica-coated powder E (hereinafter referred to simply as "silica-titania powder E"). The silica-titania-coated powder E obtained was excellent in dispersed state.

Fourth Layer: Titania Coating:

A container containing 100 ml of deionized water was heated in an oil bath while keeping the oil temperature at 80° C. Into the heated deionized water was dispersed 10 g of the silica-titania-coated powder E. A solution prepared by mixing 100 ml of ethanol with 11 g of titanium tetrachloride was added dropwise over 60 minutes to the dispersion under stirring.

After the dropwise addition, a decomposition reaction for film formation was conducted for 2 hours while maintaining the temperature at 80° C.

After completion of the reaction, the solid matter was taken out by filtration and washed with a sufficient amount of distilled water and finally with ammonia water to adjust the pH to 8. Thereafter, 200 ml of ethanol was added to wash the solid matter, which was then dried in a vacuum dryer.

The thus-obtained silica-titania powder F, which had a titania coating as the fourth layer, had a spectral reflection curve having a peak wavelength of 780 nm, with a reflectance of 56%. It was a red-purple powder.

INDUSTRIAL APPLICABILITY

According to the present invention, a technique for using inexpensive aqueous metal salt solutions as materials for metal oxide coating films has been developed. As a result, powders coated with metal oxide films can be produced at low cost and are hence usable in a wider range of applications than conventional ones.

Since a powder coated with a multilayered metal oxide film having an excellent function can also be produced at low cost, it can be a general-purpose powder.

The technique of forming a metal oxide coating film from a metal alkoxide is applicable also to powders made of metals or plastics susceptible to corrosion by acids. By using this technique to form the first layer only, less expensive aqueous metal salt solutions can be used for forming the second and any overlying coating layers. The thus-coated powders can hence be used in a wider range of applications than conventional ones.

According to the present invention, a magnetic color toner having light resistance and a technique for producing the same can be provided.

By forming a multilayered interference coating on glass beads, a magnetic color toner or a magnetic color ink can be

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produced without necessitating any coloring agent. The coated beads provide a distinctive retroreflective pigment.

What is claimed is:

1. A multilayer-coated powder, wherein at least one layer of the multilayer comprises a metal hydroxide film or a metal oxide film formed by hydrolysis of a metal alkoxide having thereon a coating film comprising a metal hydroxide film or a metal oxide film formed by a reaction of a metal salt in an aqueous solution.

2. The multilayer-coated powder according to claim 1, wherein the metal hydroxide or the metal oxide film formed by the hydrolysis of a metal alkoxide is heated.

3. The multilayer-coated powder according to claim 1 or 2, wherein the metal hydroxide or the metal oxide film formed by the reaction of a metal salt in an aqueous solution is heated after the formation.

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4. A process for producing a multilayer-coated powder, which comprises: forming a metal hydroxide film or a metal oxide film as at least one layer of a multilayered film by hydrolysis of a metal alkoxide; and forming thereon a coating film of a metal hydroxide film or a metal oxide film by a reaction of a metal salt in an aqueous solution.

5. The process for producing a multilayer-coated powder according to claim 4, wherein the metal hydroxide film or the metal oxide film is formed by the hydrolysis of a metal alkoxide, and then heated.

6. The process for producing a multilayer-coated powder according to claim 4 or 5, wherein the metal hydroxide film or the metal oxide film is formed by the reaction of a metal salt in an aqueous solution, and then heated.

* * * * *



US006110633A

United States Patent [19][11] **Patent Number:** **6,110,633****Atarashi et al.**[45] **Date of Patent:** **Aug. 29, 2000**[54] **COLOR MAGNETIC TONER AND PROCESS
FOR PRODUCING THE SAME**[58] **Field of Search** 430/45, 106.6,
430/137; 428/403[75] **Inventors:** Takafumi Atarashi; Tokyo, Japan;
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Moniwadai 4-chome, Taihaku-ku,
Sendai-shi, Miyagi, Japan[56] **References Cited****U.S. PATENT DOCUMENTS**4,758,490 7/1988 Kitabatake 430/106.6
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5,763,085 6/1998 Atarashi et al. 428/403[73] **Assignees:** Nittetsu Mining Co., Ltd., Tokyo,
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& Seas, PLLC[21] **Appl. No.:** **09/202,194**[22] **PCT Filed:** **Jun. 6, 1997**[86] **PCT No.:** **PCT/JP97/01941**§ 371 Date: **Mar. 29, 1999**§ 102(e) Date: **Mar. 29, 1999**[87] **PCT Pub. No.:** **WO98/05605****PCT Pub. Date:** **Feb. 12, 1998**[30] **Foreign Application Priority Data**

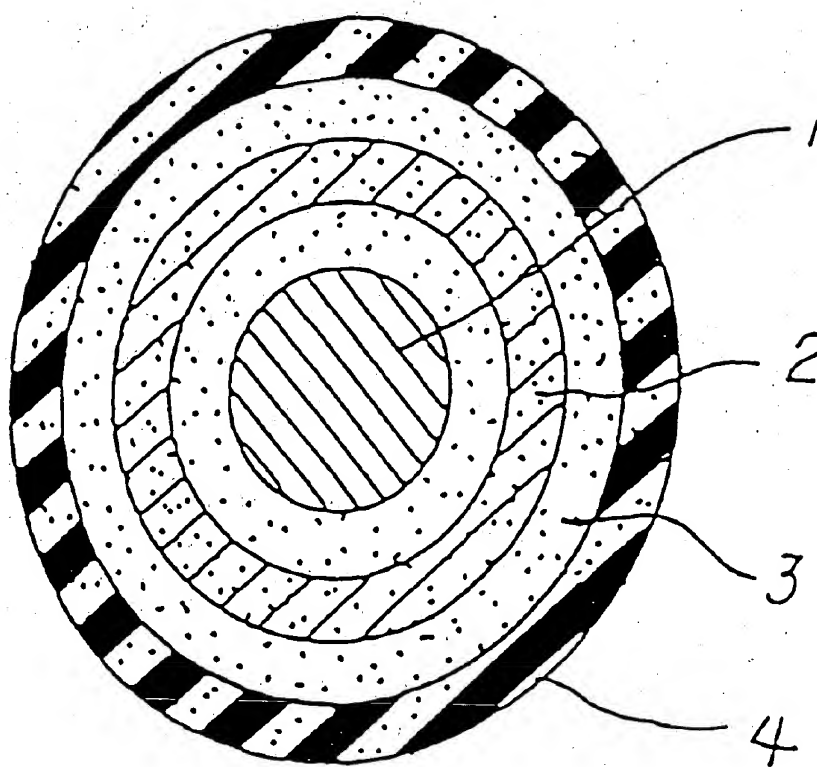
Jun. 10, 1996 [JP] Japan 8-147420

[51] **Int. Cl.⁷** **G03G 9/083**[52] **U.S. Cl.** **430/106.6; 430/137**[57] **ABSTRACT**

It is to provide a powder for use as a raw material for color magnetic toners for use in a color copier or the like which have been colored vividly as well as in white, and a dry color magnetic toner which is obtained from the raw material. The dry color magnetic toner comprises a powder comprising a light-interference multilayered film formed on a magnetic particle and at least one organic polymer coating film or a colored film on the surface of the powder. The process for producing the dry color magnetic toner comprises coating the surface of the powder having thereon a light-interference multilayered film with at least one organic polymer coating film.

5 Claims, 1 Drawing Sheet

FIG. 1



COLOR MAGNETIC TONER AND PROCESS FOR PRODUCING THE SAME

TECHNICAL FIELD

The present invention relates to a composite powder for use as a raw material for color magnetic toners, color magnetic inks, or the like, and relates to a process for producing the composite powder.

BACKGROUND ART

The electrophotographic image-forming methods currently used in copying, printing, etc. include a two-component development method in which a magnetic carrier and a toner as a colorant are used in combination, and a one-component development method which uses a toner which itself is magnetic.

Because of the nonuse of a carrier, the one-component development method has many advantages, for example, that the development apparatus is simple (the sizes of the development apparatuses are about a half to one-third the sizes of those used in the two-component development method), and that the management of developers is easy. However, when this method is used for forming color images, darkish magnetic toners should be used and images of vivid colors cannot be obtained.

The reason for this is as follows. In order to obtain clear color images by the one-component development method, magnetic toners themselves should be colored vividly. However, since the magnetic material particles serving as the bases thereof are generally black, merely forming a colored film directly on the surface of such base particles results in a dark color as a whole.

Accordingly, the two-component development method is employed at present for forming color images. However, since color copying necessitates four colors, i.e., three primary colors and black, a larger development apparatus is necessary as a matter of course.

Additionally, there are problems concerning the management of developers, the treatment of carriers resulting from development, etc.

Consequently, if vivid colors are obtainable by the one-component development method, the use of this method is preferred because the copier is simple and compact and the problems concerning the management of developers and the treatment of carriers are eliminated. However, magnetic toners for the one-component development method which are suitable for the formation of color images have not been obtained so far.

Under these circumstances, the present inventors previously proposed: a method which comprises dispersing a base particle into a metal alkoxide solution and hydrolyzing the metal alkoxide to thereby form on the surface of the base particle a metal oxide film having a uniform thickness of 0.01 to 20 μm (Unexamined Published Japanese Patent Application No. 6-228604); a functional powder having thereon plural layers of a metal oxide thin film and a metal thin film alternatively (Unexamined Published Japanese Patent Application No. 7-90310); and a process comprising heating a powder coated with a multilayered metal oxide film to thereby produce a powder having a multilayered metal oxide film which is denser and more stable (WO96/28169).

The above-described powder having plural layers of a metal oxide film or a metal film can be made to have a special function by regulating the thickness of each film. For

example, when coating films having different refractive indexes are formed on the surface of the base particle in a thickness corresponding to one-fourth the wavelength of an incident light, then a powder which reflects all of the incident light is obtained. This suggests the possibilities that by applying the above technique to the base particle of a magnetic material, a magnetic powder for magnetic toners might be produced which wholly reflects light and has a vivid white color, and that further forming a colored layer on the surface of this magnetic powder and then forming a resin layer thereon might yield a color magnetic toner colored vividly.

Accordingly, an object of the present invention is to further develop the above-described techniques proposed by the present inventors to thereby provide a color magnetic toner with which a vivid color is obtained even by the one-component development method.

DISCLOSURE OF THE INVENTION

The above object has been accomplished with the following toners according to the present invention:

(1) A color magnetic toner comprising a base particle of a magnetic material, wherein a light-interference multilayered film is formed on the base particle, and an organic polymer film is formed on the light-interference multilayered film;

(2) The color magnetic toner according to the above (1), wherein the light-interference multilayered film reflects light in the visible region;

(3) The color magnetic toner according to the above (1) or (2), wherein the organic polymer film contains a coloring agent;

(4) The color magnetic toner of any one according to the above (1) to (3), wherein the light-interference multilayered film comprises plural layers of a metal compound film and/or a metal film.

The similar object has been accomplished also with the following process according to the present invention:

(5) A process for producing a color magnetic toner, comprising: forming a multilayered film comprising a metal compound and/or a metal on a particle of a magnetic material; and then forming an organic polymer film by a polymerization method.

According to the constitutions described above, a color magnetic toner which, even if used as a one-component system, is capable of forming an image of a vivid color can be provided by forming a light-interference multilayered film comprising a metal compound and/or a metal on a magnetic material particle to give a powder of white or another desired color according to the film constitution and further forming thereon an organic polymer film as a binder.

By incorporating a coloring agent into the organic polymer film, a more vivid color can be obtained.

The color magnetic toner according to the present invention will be explained below in detail based on preferred embodiments thereof.

The magnetic material particle which serves as the base of the color magnetic toner of the present invention can be used as a magnetic material particle conventionally used as the base of magnetic toners. Typical examples thereof include powders of metals, such as iron, cobalt, and nickel, powders of alloys thereof, and powders of magnetic sinters, such as iron nitride.

However, it is preferred to use a magnetic material having a high magnetization because a magnetic material particle of

a smaller size tends to be used so as to heighten resolution. Preferred is a magnetic material which has a magnetization of 90 emu/g or more, preferably 150 emu/g or more, when a magnetic field of 10 kOe is applied to the powdered magnetic material. A magnetic material having such a high magnetization can give a raw-material powder giving a color magnetic toner which as a whole has a magnetization as high as from 10 to 90 emu/g (upon application of a magnetic field of 10 kOe) even when it contains a binder resin, a charge regulator, a coloring agent, etc.

The shape of the magnetic material particle may have any of isotropic shapes, such as sphere, nearly spherical shapes, and regular polyhedrons; polyhedrons, such as rectangular parallelepipeds, spheroids, rhombohedrons, plates, and prisms; and amorphous shapes.

In order to obtain a color magnetic toner having a vivid color in the present invention, it is necessary to color the magnetic material particle in white or another vivid color. For attaining this, a multilayered film having the property of causing light interference is formed on the magnetic material particle.

The light-interference multilayered film is constituted by superposing many thin films of a metal or metal compound. In forming the multilayered film, a function of reflecting or absorbing incident light in a specific wavelength range can be imparted by regulating the thickness of each film or changing the sequence of film superposition or the combination of films. Thus, the magnetic material particles can be colored white or in another vivid color.

Examples of the metal compound used for forming the multilayered film include metal oxides, metal sulfides, metal selenides, metal tellurides, and metal fluorides. Specific examples thereof include zinc oxide, aluminum oxide, cadmium oxide, titanium oxide, zirconium oxide, tantalum oxide, silicon oxide, antimony oxide, neodymium oxide, lanthanum oxide, bismuth oxide, cerium oxide, tin oxide, magnesium oxide, lithium oxide, lead oxide, cadmium sulfide, zinc sulfide, antimony sulfide, cadmium selenide, cadmium telluride, calcium fluoride, sodium fluoride, trisodium aluminum fluoride, lithium fluoride, and magnesium fluoride.

Preferred examples of the metal include silver, cobalt, nickel, iron, and alloys thereof.

Methods for forming the light-interference multilayered film will be explained below.

Usable film-forming methods for both of the metal compound film and the metal film are vapor-phase vapor deposition methods, such as PVD, CVD, and spray drying methods, in which the metal film or metal compound film is vapor-deposited directly on the surface of a magnetic material particle.

With respect to the metal film, the so-called chemical plating method can also be used, in which a magnetic material particle is placed in an aqueous metal salt solution and the metal salt in the solution is reduced to deposit the metal on the surface of the magnetic material particle.

With the current trend toward size reduction in magnetic toners and in magnetic material particles for meeting the desire for higher resolution, it has become necessary to form a uniform film on the surface of a magnetic material particle. With respect to the metal oxide, in particular, the film-forming method previously proposed by the present inventors in Unexamined Published Japanese Patent Application No. 6-228604 or 7-90310 or WO96/28169 is preferred.

Specifically, the proposed method comprises dispersing a magnetic material particle into a metal alkoxide solution,

hydrolyzing the metal alkoxide to form a uniform thin film of a metal oxide on the surface of the magnetic material particle, drying the coated particle, and repeating these steps. If necessary, steps for forming a thin metal film may be conducted before or after repetitions of those steps for forming a metal oxide film or between repetitions thereof. Thus, a multilayered film comprising metal oxide films alone or a metal oxide film and a metal film can be obtained. The metal alkoxide is selected from alkoxides of zinc, aluminum, cadmium, titanium, zirconium, tantalum, silicon, antimony, neodymium, lanthanum, bismuth, cerium, tin, magnesium, lithium, and lead.

By heating the multilayered film, the reflectance thereof can be heightened or the multilayered film can be made to be denser and more stable.

Besides being used for metal oxide film formation, this metal alkoxide method is applicable to the formation of metal sulfide films.

In thus forming metal compound films or metal films, the magnetic material particles can be colored in a desired tint by regulating the thickness of each film. For example, when thin films of metal compounds having different refractive indexes are formed each in a thickness corresponding to one-fourth the wavelength of an incident light, the magnetic material particles can be made to reflect all of the incident light and hence have a white color.

Consequently, the thickness of each film of the light-interference multilayered film and the total thickness of the multilayered film are determined so that the magnetic material particles assume a desired color.

An organic polymer film serving as a binder is formed on the surface of the multilayer coated-magnetic material particles. Thus, a color magnetic toner colored vividly is obtained.

For forming an organic polymer film, the PVD, CVD, or spray drying method or the like can be used to directly coat the surface of the multilayer coated-magnetic material particles with an organic polymer film. It is, however, preferred in the present invention to use a polymerization method for the film formation so as to enhance adhesion.

A preferred polymerization method can be suitably selected according to the kind of the organic polymer. Specifically, an emulsion polymerization method, a suspension polymerization method, a seed polymerization method, an in situ polymerization method, and the like can be employed according to the kinds of organic polymers. For some kinds of organic polymers, a phase separation method can also be employed.

Organic polymers for use as binder resins for magnetic toners can be used without particular limitations, as long as films of these polymers can be formed by any of the polymerization methods enumerated above. For example, the following polymers are usable.

Examples of the usable organic polymers include oligomers and polymers of aromatic hydrocarbons (for example, polystyrene, styrene- α -methylstyrene copolymers, styrene-vinyltoluene copolymers); olefin oligomers and polymers (for example, polypropylene, polyethylene, polybutene); vinyl oligomers and polymers comprising copolymers of monomers (for example, ethyl acrylate, methyl methacrylate, ethyl methacrylate, acrylonitrile, polyacrylic acid, polymethacrylic acid, vinyl acetate); oligomers alone (for example, diene oligomers, such as polybutadiene, polypentadiene, and polychloroprene; and ester oligomers, such as polyesters, and copolymers of these oligomers); copolymers made up of two or more of the above monomers

and oligomers (for example, hydrocarbon monomers and oligomers, olefin oligomers, vinyl monomers and oligomers, polychloroprene monomers and oligomers, and ester monomers and oligomers); waxes (for example, natural waxes, polyethylene wax); and alkyl resins (for example, rosin-modified alkyl resins).

The organic polymer film is formed in such an amount that when the color magnetic toner is deposited on a paper surface, the polymer film spreads to prevent the toner particles from falling or separating from the paper surface. However, from the standpoint of relationship with the coloring agent described below, the organic polymer film coating is preferably formed in such an amount that when the toner is deposited on a paper surface, the organic polymer spreads over an area about four times the area occupied by the magnetic material particles.

The color magnetic toner of the present invention is characterized in that the toner itself has a vivid color because the light-interference multilayered film formed on the magnetic material particle causes an incident light to undergo interference and thus assumes a color. Consequently, an organic polymer film functioning only as a binder is sufficient, and it may be transparent. However, since deposition of the color magnetic toner on a paper surface may result in uncolored areas due to spaces among magnetic material particles, it is preferred to incorporate a coloring agent into the organic polymer film so that the spread organic polymer film resulting from toner deposition is utilized to color the areas surrounding the deposited toner.

Examples of the coloring agent used for coloring the organic polymer film include yellow, magenta, and cyan coloring agents. The following organic dyes and organic pigments can be used for each color.

Organic Dyes:

- a. Yellow: monoazo dyes, azomethine dyes, oil dyes, etc.
- b. Magenta: thioindigo dyes, xanthene dyes, 2,9-quinacridone dyes, oil dyes, etc.
- c. Cyan: copper phthalocyanine dyes, oil dyes, etc.

Organic Pigments:

- a. Yellow: bisazo pigments, benzidine pigments, phorone yellow pigments, etc.
- b. Magenta: quinacridone pigments, anthraquinone pigments, rhodamine pigments, naphthol type insoluble azo pigments, etc.
- c. Cyan: phthalocyanine pigments, etc.

These coloring agents may be contained in the organic polymer film preferably in such an amount that when the color magnetic toner is deposited on a paper surface, coloring with the coloring agents is possible evenly over an area about 2 to 10 times the projected area of the magnetic material particles.

The color magnetic toner of the present invention comprises the magnetic material particle, the light-interference multilayered film, and the organic polymer film described above as essential components. Besides these, the toner may further contain a charge regulator, a fluidizing agent, and a surface lubricant incorporated in the organic polymer film.

The charge regulator is an additive added for regulating the electrification characteristics of the color magnetic toner. Usable as the charge regulator are organic acids, surfactants, and dielectric substances. Examples of charge regulators usable for toners of the positive electrification type include metal complexes of alkylsalicylic acids, metal complexes of dicarboxylic acids, metal salts of polycyclic salicylic acids, and metal salts of fatty acids. Examples of charge regulators usable for toners of the negative electrification type include

quaternary ammonium salts, benzothiazole derivatives, guanamine derivatives, dibutyltin oxide, nitrogen-containing compounds, chlorinated paraffins, and chlorinated polyesters.

The fluidizing agent is an additive added for improving the flowability of the color magnetic toner to thereby prevent unnecessary toner particles from remaining on a paper surface. Examples include colloidal silica, aerosil, titanium oxide powder, alumina powder, zinc oxide powder, and powder of a fatty acid metal salt.

The surface lubricant is an additive added for preventing the color magnetic toner from adhering to the fixing roll or other parts of a developing machine. Examples include low molecular polyethylene, and low molecular polypropylene.

The upper limit of the content of these additives in the organic polymer film is preferably about 60% by weight in terms of a total amount. If the content of the additives exceeds the upper limit, practical magnetic properties as a color magnetic toner cannot be obtained.

By combining the elements described above, a color magnetic toner having a vivid color can be obtained.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a diagrammatic sectional view illustrating one embodiment of the color magnetic toner according to the present invention. As shown in the figure, this particle consists of: a magnetic material particle 1 as a base particle; a light-interference multilayered film formed on the base particle and comprising a metal compound film 2 and another metal compound film 3 superposed thereon; and an organic polymer film 4 with which the outermost surface is covered. One of the metal compound film 2 and the metal compound film 3 may be a metal film.

BEST MODES FOR CARRYING OUT THE INVENTION

The present invention can be understood more clearly by reference to the following Examples and Comparative Example. However, the invention should not be construed as being limited by the following Examples.

EXAMPLE 1

Process for Producing Oxide-coated Powder

First layer: Silica coating:

Into 100 ml of ethanol was dispersed 10 g of a carbonyl iron powder (average particle diameter, 1.8 μm) manufactured by BASF. The container was heated in an oil bath to keep the liquid temperature at 55° C. Thereto were added 6 g of silicon ethoxide, 6 g of ammonia water (29%), and 8 g of water. This mixture was allowed to react for 2 hours under stirring. After the reaction, the reaction mixture was diluted and washed with ethanol and filtered. The solid matter was dried in a vacuum dryer at 110° C. for 3 hours. After the drying, the resultant powder was heated with a rotary tubular oven at 650° C. for 30 minutes to obtain silica-coated powder A.

The film thickness of the silica-coated powder A obtained was 75 nm. This powder had excellent dispersibility.

Second layer: Titania coating:

After the heating, 10 g of the silica-coated powder A obtained was redispersed into 200 ml of ethanol. The container was heated in an oil bath to keep the liquid temperature at 55° C. Thereto was added 5 g of titanium ethoxide. This mixture was stirred. A solution prepared by mixing 30 ml of ethanol with 8.0 g of water was added dropwise to the above mixture over 60 minutes, and the

resultant mixture was allowed to react for 2 hours. The particles were then dried in vacuo and heated to obtain silica-titania-coated powder B.

The silica-titania-coated powder B obtained had satisfactory dispersibility and was an independent particle. The titania film of this silica-titania-coated powder B had a thickness of 50 nm.

This powder had a spectral reflection curve having a peak wavelength of 445 nm and had a reflectance at the peak wavelength of 40%. It was vivid blue.

Polystyrene Composite Powder

To 600 g of distilled water was added 500 g of styrene monomer. While this mixture was heated to 70° C. under stirring, sodium lauryl sulfate was added thereto to emulsify the monomer. Subsequently, 25 g of the silica-titania-coated powder B whose surface had been lipophilized with methacrylic acid was added to the emulsion. The resultant mixture was stirred at a high speed to sufficiently mix the ingredients.

A 10% aqueous ammonium persulfate solution was added thereto to initiate a polymerization reaction. The mixture was allowed to react for 4 hours under stirring. After completion of the reaction, the reaction mixture was diluted with 2 liters of distilled water, and the supernatant was discarded by decantation to collect the precipitate. This precipitate was dried on a filter paper to obtain a blue polystyrene-coated powder.

The blue polystyrene-coated powder obtained had a spherical particle shape and had a magnetization of 120 emu/g in a magnetic field of 10 kOe.

EXAMPLE 2

First layer: Silica coating:

Into 100 ml of ethanol was dispersed 10 g of a carbonyl iron powder (average particle diameter, 1.8 μ m) manufactured by BASF. The container was heated in an oil bath to keep the liquid temperature at 55° C. Thereto were added 6 g of silicon ethoxide, 6 g of ammonia water (29%), and 8 g of water. This mixture was allowed to react for 2 hours under stirring. After the reaction, the reaction mixture was diluted and washed with ethanol and filtered. The solid matter was dried in a vacuum dryer at 110° C. for 3 hours. After the drying, the resultant powder was heated with a rotary tubular oven at 650° C. for 30 minutes to obtain silica-coated powder B.

The film thickness of the silica-coated powder B obtained was 70 nm. This powder had excellent dispersibility.

Second layer: Titania coating:

After the heating, 10 g of the silica-coated powder B obtained was redispersed into 200 ml of ethanol. The container was heated in an oil bath to keep the liquid temperature at 55° C. Thereto was added 4.7 g of titanium ethoxide. This mixture was stirred. A solution prepared by mixing 30 ml of ethanol with 8.0 g of water was added dropwise to the above mixture over 60 minutes, and the resultant mixture was allowed to react for 2 hours. The particles were then dried in vacuo and heated to obtain silica-titania-coated powder C.

The silica-titania-coated powder C obtained had satisfactory dispersibility and was an independent particle. The titania film of this silica-titania-coated powder C had a thickness of 45 nm.

This powder had a spectral reflection curve having a peak wavelength of 410 nm and had a reflectance at the peak wavelength of 41%. It was vivid violet.

Third layer: Silica coating:

Into 100 ml of ethanol was dispersed 10 g of the silica-titania-coated powder C. The container was heated in an oil bath to keep the liquid temperature at 55° C. Thereto were added 6 g of silicon ethoxide, 6 g of ammonia water (29%), and 8 g of water. This mixture was allowed to react for 2 hours under stirring. After the reaction, the reaction mixture was diluted and washed with ethanol and filtered. The solid matter was dried in a vacuum dryer at 110° C. for 3 hours. After the drying, the resultant powder was heated with a rotary tubular oven at 650° C. for 30 minutes to obtain silica-titania-silica-coated powder D.

The film thickness of the silica-titania-silica-coated powder D obtained was 75 nm. This powder had excellent dispersibility.

Fourth layer: Titania coating:

After the heating, 10 g of the silica-titania-silica-coated powder D obtained was redispersed into 200 ml of ethanol. The container was heated in an oil bath to keep the liquid temperature at 55° C. Thereto was added 5.5 g of titanium ethoxide. This mixture was stirred. A solution prepared by mixing 30 ml of ethanol with 8.0 g of water was added dropwise to the above mixture over 60 minutes, and the resultant mixture was allowed to react for 2 hours. The particles were then dried in vacuo and heated to obtain silica-titania-silica-titania-coated powder E.

The silica-titania-silica-titania-coated powder E obtained had satisfactory dispersibility and was an independent particle. The newly formed titania film of this silica-titania-silica-titania-coated powder E had a thickness of 53 nm.

Polystyrene Composite Powder:

To 600 g of distilled water were added 90 g of styrene monomer and 10 g of butylene acrylate. While this mixture was heated to 70° C. under stirring, sodium lauryl sulfate was added thereto to emulsify the monomers.

Subsequently, 50 g of the silica-titania-silica-titania-coated powder E was added to the emulsion. The resultant mixture was stirred at a high speed to sufficiently mix the ingredients.

A 10% aqueous ammonium persulfate solution was added thereto to initiate polymerization reactions. The mixture was allowed to react for 4 hours under stirring. After completion of the reactions, the reaction mixture was diluted with 2 liters of distilled water, and the supernatant was discarded by decantation. The precipitate was dried on a filter paper to obtain a blue polystyrene-coated powder.

The polystyrene-coated powder obtained had a spectral reflection curve having a peak wavelength of 445 nm and had a reflectance at the peak wavelength of 55%. It was vivid blue. This powder had a magnetization of 78 emu/g in a magnetic field of 10 kOe.

COMPARATIVE EXAMPLE 1

Mere Mixture of Magnetic Material and Pigment

Turkey blue (blue pigment) (average particle diameter, 0.2 μ m; reflection peak, 455 μ m; reflectance, 55%) was mixed with a carbonyl iron powder (average particle diameter, 1.8 μ m) manufactured by BASF, in a weight ratio of 25 g:25 g. This mixture was sufficiently homogenized.

This powder was added to 600 g of distilled water together with 90 g of styrene monomer and 10 g of butylene acrylate. The resultant mixture was heated to 70° C. under stirring. Sodium lauryl sulfate was further added thereto to emulsify the monomers, and this mixture was stirred at a high speed to sufficiently mix the ingredients.

A 10% aqueous ammonium persulfate solution was added thereto to initiate polymerization reactions. The mixture was allowed to react for 4 hours under stirring.

After completion of the reactions, the reaction mixture was diluted with 2 liters of distilled water, and the supernatant was discarded by decantation. The precipitate was dried on a filter paper. As a result, spherical particles were obtained each composed of pigment and iron particles wholly covered with polystyrene and united with each other.

This polystyrene-coated powder A was dark-blue and had a reflection peak at 455 nm and a reflectance reduced to 22%. This powder had a magnetization of 75 emu/g in a magnetic field of 10 kOe.

As apparent from a comparison between Example 2 and Comparative Example 1, it was ascertained that the mere mixing of a pigment with magnetic material particles and a binder resin does not result in an improved color, and that in order for a color magnetic toner having the same magnetization to be superior in color, the magnetic material particles themselves should be colored as in Example 2.

EXAMPLE 3

In 20 g of benzene was dissolved 10 g of oil blue as an organic dye. This solution was mixed with 90 g of styrene monomer and 10 g of butylene acrylate to obtain a starting material for a colored resin.

The above starting material for a colored resin was added to 600 g of distilled water. Thereto was added sodium lauryl sulfate. This mixture was heated to 70° C. under stirring and emulsified.

Subsequently, 50 g of a silica-titania-coated powder E prepared in the same manner as in Example 2 was added to the resultant solution, and this mixture was stirred at a high speed to sufficiently mix the ingredients.

A 10% aqueous solution of ammonium persulfate was added thereto to conduct a polymerization reaction for 5 hours. After completion of the reaction, the reaction mixture was diluted twice with 2 liters of distilled water and washing with decantation. The precipitate was filtrated and washed to obtain blue polystyrene-coated powder B.

The polystyrene-coated powder B obtained had a spectral reflection curve having a peak wavelength of 455 nm and had a reflectance at the peak wavelength of 52%. This polystyrene-coated powder B had a magnetization of 75 emu/g in a magnetic field of 10 kOe.

Using a coater, the polystyrene-coated powders A and B obtained in Example 3 and Comparative Example 1 each was evenly applied in an amount of 1.7 g on an A4 paper sheet for copying over 80% of its area. As a result, the polystyrene-coated powder B obtained in Example 3 colored

the paper vivid blue. On the other hand, the polystyrene-coated powder A obtained in Comparative Example 1 colored the paper dark-gray.

INDUSTRIAL APPLICABILITY

As described above, a color magnetic toner which, even if used as a one-component system, can form images of a vivid color can be provided according to the present invention by forming a light-interference multilayered film comprising plural layers of a metal compound layer and/or a metal layer on a magnetic material particle to give a powder of white or another desired color according to the film constitution and further forming thereon an organic polymer film as a binder.

By incorporating a coloring agent into the organic polymer film, a more vivid color can be obtained.

As a result, copiers can be made simpler and more compact, and color printing is possible also in laser printers or facsimile telegraphs employing the same principle. Furthermore, since the color magnetic toner is free from the carrier waste discard associated with the two-component development method, it not only attains a cost reduction but also is advantageous in environmental conservation.

What is claimed is:

1. A color magnetic toner comprising a base particle of a magnetic material, a light-interference multilayered film formed on the base particle, and an organic polymer film formed on the light-interference multilayered film, wherein said light-interference multilayered film has a color other than white and said organic polymer film is transparent.

2. The color magnetic toner according to claim 1, wherein the light-interference multilayered film reflects light in the visible region.

3. The color magnetic toner according to claim 1 or 2, wherein the organic polymer film contains a coloring agent.

4. The color magnetic toner of any one according to claims 1 to 3, wherein the light-interference multilayered film comprises plural layers of a metal compound film and/or a metal film.

5. A process for producing a color magnetic toner, comprising: forming a multilayered film comprising a metal compound and/or a metal on a particle of a magnetic material; and then forming an organic polymer film by a polymerization method, wherein said light-interference multilayered film has a color other than white and said organic polymer film is transparent.

* * * * *

United States Patent [19]

Murphy et al.

[11] Patent Number: 4,820,518

[45] Date of Patent: Apr. 11, 1989

[54] COSMETIC POWDER PRODUCT

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[21] Appl. No.: 940,431

[22] Filed: Dec. 11, 1986

[51] Int. Cl.⁴ A61K 6/00; B29B 9/00

[52] U.S. Cl. 424/401; 424/63;
424/486; 264/7

[58] Field of Search 428/405; 427/219, 221;
424/63, 69, 401, 489, 486, 502; 264/7

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[57] ABSTRACT

A non-pressed cosmetic powder containing hydrophobic inorganic pigments.

13 Claims, No Drawings

COSMETIC POWDER PRODUCT

BACKGROUND OF THE INVENTION

In the past, loose powder cosmetic products were commonly applied to the skin through use of a puff. More recently, pressed powder products, such as face powder, eye shadow, blushes or the like have replaced the loose powder products and are produced by compressing loose powder into a metal pan using direct pressure. The pan containing the pressed powder cake is then glued into a compact or other container.

In the fabrication of pressed powder products, the pressure used in the pressing operation must be maintained within precise limits. If the pressure is too great, the metal pan may be distorted and must be discarded. In addition, utilizing a high pressure results in a cake which lacks the desired payoff characteristics. On the other hand, if the pressure is too low, the pressed cake will lack cohesive strength.

Further, certain powder compositions cannot be successfully used as a pressed powder cake because the pressure required to obtain the necessary cohesive strength will either distort the metal pan or produce a cake that is so hard that it lacks payoff.

To eliminate the problems associated with pressed powder products, non-pressed or poured powder cosmetic products have been proposed, as disclosed in U.S. Pat. Nos. 4,337,859 and 4,414,200. To form a non-pressed cosmetic product, a slurry is initially formed by mixing powdered materials, a binder such as a fatty acid, an evaporable carrier and pigments. The slurry is then poured into a container or mold, and on cooling and evaporation of the carrier, a solid product or cake is produced.

The powder cake, as produced by the aforementioned patents, can be formed directly in the compact or marketing container without the use of a metal pan as is required in pressed powder processes. By eliminating the use of the metal pan, the design configuration of the cake can be increased and the labor and assembly operations are greatly reduced.

It has been noted that certain inorganic pigments, such as the oxides of iron, chromium and magnesium, possess a high degree of static charge. In a pressed powder product, the static charge does not present problems since the binders used in the pressed powder formulation tend to disperse the charges and the mechanical force of compression tends to hold the cake together.

However, in a non-pressed powder product, as disclosed in the aforementioned patents, the static charge on the pigments can cause color drift during filling and cracking of the cake on drying. These problems are further accentuated when small amounts of water from condensed steam used in the manufacturing process are present in the composition. It has been found that pigments tainted with water are attracted to various parts of the manufacturing equipment, such as the kettle, agitators and filling equipment, with the result that the slurry being poured into the mold or container does not contain all of the pigments of the formulation and shade drift or lack of color can occur when using multiple color pigments.

SUMMARY OF THE INVENTION

The invention is directed to a non-pressed cosmetic powder product containing hydrophobic inorganic

pigments which resist color drift and prevent cracking of the cake during drying. The product is formed by mixing cosmetically acceptable powders, a binder, such as a fatty alcohol containing from 12 to 22 carbon atoms, an evaporable carrier and hydrophobic inorganic pigments to form a slurry. The hydrophobic pigments are formed by coating the inorganic pigments with a non-polar, water insoluble, organic coating, such as a polymethylsilicone.

The slurry at an elevated temperature is poured into a mold or container, and on cooling and evaporation of the carrier, a solid powder cake is produced.

The hydrophobic coating on the pigments eliminates static charges and thereby produces a dry powder cake that is homogeneous in composition.

The use of the hydrophobic pigments also eliminates color drift and provides a more predictable color in the final product.

Other objects and advantages will appear in the course of the following description.

DESCRIPTION OF THE PREFERRED EMBODIMENT

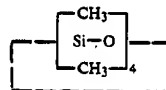
The cosmetic powder product of the invention is prepared from a slurry having the following formulation in weight percent:

Finely divided inert filler or powder	70%-10%
Binder	5%-30%
Volatile carrier	25%-60%
Cosmetic coloring materials	1%-15%

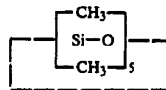
The finely divided filler or powder can take the form of cosmetically acceptable powders such as aluminum hydroxide, kaolin, talc, mica, corn starch, calcium carbonate, silicon dioxide, calcined clay, barium sulfate, aluminum oxide, aluminum silicate, and the like.

The binder is preferably a fatty alcohol that is miscible with the carrier and contains from 12 to 22 carbon atoms in the molecule. The fatty alcohol can preferably take the form of cetyl alcohol, stearyl alcohol, and the like.

The volatile organic carrier is a liquid at room temperature and preferably takes the form of a siloxane composed primarily of two cyclic components: D₄ cyclodimethicone and D₅ cyclodimethicone. The D₄ component represents the majority with the D₅ being a minor constituent. Chemically D₄ cyclodimethicone may be symbolically written as:



and D₅ cyclodimethicone may be symbolically written as:



The cosmetically acceptable coloring materials include inorganic pigments such as iron oxide, ultrama-

oxides, chromium oxide, chromium hydroxide, titanium dioxide, ferric ferrocyanide, and ferric ammonium ferrocyanide. In addition, the coloring materials can also include organic dyes and lakes and pearlescents.

It has been found that the inorganic pigments normally have a high degree of static charge. In a non-pressed product, as in the invention, the static charge on the inorganic pigments can cause color drift and cracking of the dried cake. In accordance with the invention, these problems are eliminated by coating the inorganic pigments with a non-polar, water insoluble, dielectric material which renders the pigments hydrophobic and eliminates the static charge. The preferred material for coating the inorganic pigments is a polymethylsilicone such as dimethylmethicone. Other coating materials which can be employed are metallic soaps, such as aluminum myristate and aluminum laurate; amino acids such as acylglutamate; oils such as mineral oil; lecithin and the like. The hydrophobic coating is used in an amount of 1% to 3% by weight of the inorganic pigments.

It has been proposed in the past to incorporate anti-frictional materials, such as polymethylsilicones, in cosmetic products to provide a smooth feel on application to the skin. However, the polymethylsilicone is used for a different purpose in the composition of the invention in that it provides a hydrophobic coating on the inorganic pigment particles to eliminate the static charge and prevent hydration as well as agglomeration of the particles. In the present composition, the fatty alcohol imparts smoothness and slip to the composition.

In addition to the above ingredients, the slurry can also contain small amounts, up to 2% by weight, of fatty acid esters containing from 12 to 22 carbon atoms such as isopropyl myristate or isopropyl palmitate which prevent dusting of the cake, and/or magnesium stearate which aids in preventing glazing of the cake, and/or a preservative such as methyl paraben or propyl paraben, and/or perfumes.

To prepare the cosmetic product of the invention, a liquid slurry is prepared by dispersing the fatty alcohol in the volatile carrier at an elevated temperature, generally in the range of about 60° C. to 70° C. The remaining ingredients, such as the powdered filler, coloring materials and other additives are then mixed into the liquid dispersion to provide the slurry. The slurry, at a temperature of about 50° C. to 60° C., is then poured by gravity into a container or mold, and on cooling to a temperature below about 45° C. the slurry will solidify to form a solid cake.

Subsequently the cake is dried, preferably at an elevated temperature of about 40° C. for about 60 hours to evaporate the carrier from the cake so that the dried cake has a residual carrier content of less than 2% by weight. While it is possible to evaporate all the carrier, it is normally uneconomical to go beyond the 2% level. The resulting cake can then be packaged in a conventional manner.

The following formulations in weight percent illustrate the preparation of poured powder products in accordance with the invention:

INGREDIENTS	Example No. 1 - BLUSHER
Silicone SF 1173	38.00
Alumina 617	32.71
Stearyl Alcohol	8.50

-continued

Ethyl Hexyl Palmitate	1.00
Magnesium Stearate	1.05
Biron HB	6.30
Methyl Paraben	0.13
Propyl Paraben	0.05
Germall 115	0.08
Mineral Oil	0.43
Silicone 1107	0.03
Tenox BHA	0.01
C-19-003 D&C Red #7	0.96
Coated 9111 Cosmetic Brown	1.60
Coated 9124 Red Iron Oxide	1.39
Coated D9510 Ultramarine Blue	0.37
Mica M	5.25
Timica Pearl White	1.07
MP 1001 Pearl	1.07
	100.00%

INGREDIENTS	Example No. 2 - BLUSHER
Silicone SF 1173	38.00
Alumina 617	26.92
Stearyl Alcohol	8.50
Ethyl Hexyl Palmitate	1.00
Magnesium Stearate	1.05
Biron HB	6.30
Methyl Paraben	0.13
Propyl Paraben	0.05
Germall 115	0.08
Mineral Oil	0.43
Silicone 1107	0.03
Tenox BHA	0.01
Coated 9124 Red Iron Oxide	0.65
Mica M	5.25
MP 101 Pearl	10.94
6506 D&C Red #6	0.66
	100.00%

INGREDIENTS	Example No. 3 - EYESHADOW
Silicone SF 1173	38.00
Alumina 617	25.70
Stearyl Alcohol	8.50
Ethyl Hexyl Palmitate	1.00
Magnesium Stearate	1.05
Biron HB	2.63
Methyl Paraben	0.13
Propyl Paraben	0.05
Germall 115	0.08
Mineral Oil	1.57
Tenox BHA	0.01
Coated D9510 Ultramarine Blue	3.80
Mica M	5.83
Timica Pearl White	0.58
Coated D9146 Black Iron Oxide	2.33
Coated D9210 Manganese Violet	2.91
Cloisone Blue	5.83
	100.00%

INGREDIENTS	Example No. 4 - EYESHADOW
Silicone SF 1173	38.00
Alumina 617	21.90
Stearyl Alcohol	8.50
Ethyl Hexyl Palmitate	1.00
Magnesium Stearate	1.05
Biron HB	6.82
Methyl Paraben	0.13
Propyl Paraben	0.05
Germall 115	0.08
Mineral Oil	3.03
Tenox BHA	0.01
Coated D9510 Ultramarine Blue	0.87
Mica M	3.25
Coated D9146 Black Iron Oxide	0.11
Cloisone Blue	5.41
Coated D9310 Chromium Hydroxide Green	0.05
Flamenco Super Pearl 100	9.74
	100.00%

INGREDIENTS	Example No. 5
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Silicone SF1173	38.00
Alumina 617	10.69
Stearyl Alcohol	8.50
Ethyl Hexyl Palmitate	1.00
Magnesium Stearate	1.05
Biron HB	6.30
Methyl Paraben	0.13
Propyl Paraben	0.05
Germall 115	0.08
Tenox BHA	0.01
Silicone Coated Chromium Hydroxide Green	0.74
Amino Acid Treated Black Iron Oxide	3.18
Silicone Coated Ultramarine Blue	0.21
Amino Acid Treated Yellow Iron Oxide	1.48
Mineral Oil	3.18
Mica M	2.63
Cloisone Green	12.71
Colorona Dark Blue	10.06
	100.00%

INGREDIENTS	Example No. 6
Silicone SF1173	38.00
Alumina 617	21.47
Stearyl Alcohol	8.50
Ethyl Hexyl Palmitate	1.00
Magnesium Stearate	1.05
Biron HB	5.25
Methyl Paraben	0.13
Propyl Paraben	0.05
Germall 115	0.08
Tenox BHA	0.01
Mineral Oil	3.57
Mica M	2.63
Silicone Coated Cosmetic Brown	0.06
Metal Soap Treated Yellow Iron Oxide	0.30
Silicone 1107 Fluid	0.03
Flamenco Gold 100	17.87
	100.00%

In all of the above examples, the fatty alcohol was added to the liquid siloxane at a temperature of 65° C. and the remaining ingredients were then blended into the liquid to form a slurry. In each case the slurry, at a temperature of about 55° C. was poured into plastic molds to form the products. Air at a temperature of 28° C. was passed over the products for a period of 72 hours to evaporate the major proportion of the siloxane to provide the finished product composition. In each example the dried product had a residual siloxane content of less than 2% by weight.

In molding the product, the slurry can be poured directly into a component of the final package, or alternately, the slurry can be introduced into a separate mold or container and subsequently transferred to the package.

The product of the invention can be used to produce a wide variety of cosmetic or pharmaceutical products such as face powders, rouges, blushes, antiperspirants, eye shadows, deodorants, and the like.

Through use of the coated inorganic pigments, the pigments are hydrophobic and free of static charge so that any water associated with steam condensation during the manufacturing process will not cause color drift and a more predictable color can be achieved in the final poured powder product.

By eliminating the static charge on the inorganic pigments, a more uniform product is achieved which will not crack during the drying operation.

Various modes of carrying out the invention are contemplated as being within the scope of the following claims particularly pointing out and distinctly claiming the subject matter which is regarded as the invention.

We claim:

1. A non-pressed solid powder cosmetic product, comprising a mixture of a finely divided cosmetically acceptable filler, an organic binder, an evaporable organic carrier, and cosmetic coloring materials, said cosmetic coloring materials including inorganic pigments coated with a non-polar water insoluble organic dielectric material, said coated pigments being hydrophobic and free of static charge.
2. The product of claim 1, wherein said binder is an organic fatty alcohol containing from 12 to 22 carbon atoms and said carrier is a liquid volatile cyclic siloxane.
3. The product of claim 1, wherein said pigments are selected from the group of iron oxides, magnesium oxides, chromium oxides, and mixtures thereof.
4. A non-pressed solid powder cosmetic product, comprising a mixture of a finely divided cosmetically acceptable filler, an organic binder, an evaporable organic carrier, and cosmetic coloring materials, said cosmetic coloring materials including inorganic pigments coated with a polymethylsilicone.
5. The product of claim 4, wherein said polymethylsilicone is dimethylmethicone.
6. A non-pressed solid powder cosmetic product, comprising a mixture of a finely divided cosmetically acceptable filler, a fatty alcohol containing from 12 to 22 carbon atoms, a residual amount of an evaporable liquid cyclic siloxane, and cosmetic coloring materials including inorganic pigment particles having a static charge and coated with a non-polar water insoluble organic coating material to provide a hydrophobic static-free coating on said particles.
7. The product of claim 6, wherein said coating material comprises from 1% to 3% by weight of said particles.
8. The product of claim 6, wherein said coating material is selected from the group consisting of dimethylsilicones, metallic soaps, amino acids, oils, lecithin, and mixtures thereof.
9. A method of producing a non-pressed cosmetic powder product, comprising the steps of coating inorganic cosmetic pigment particles with an organic non-polar water insoluble coating to provide a hydrophobic substantially static free coating on said particles, mixing the coated pigment particles with a finely divided cosmetically acceptable filler, an organic binder and a liquid evaporable carrier to form a slurry, pouring the slurry into a mold to form a molded product, and evaporating the carrier while maintaining said product under atmospheric pressure to form a dried cosmetic powder product.
10. A method of producing a non-pressed cosmetic powder product, comprising the steps of coating inorganic cosmetic pigment particles with a polymethylsilicone to provide a hydrophobic substantially static free coating on said particles, mixing the coated pigment particles with a finely divided cosmetically acceptable filler, an organic binder and a liquid evaporable carrier to form a slurry, pouring the slurry into a mold to form a molded product, and evaporating the carrier while maintaining said product under atmospheric pressure to form a dried cosmetic powder product.
11. The method of claim 9, wherein said slurry is poured under atmospheric pressure into said mold.
12. The method of claim 9, wherein said inorganic pigments contain a metal selected from the group consisting of iron, magnesium, chromium and mixtures thereof.

13. A method of producing a non-pressed cosmetic powder product, comprising the steps of coating inorganic cosmetic pigment particles with an organic non-polar water insoluble coating to provide a hydrophobic substantially static free coating on said particles, mixing the coated pigment particles with a finely divided cosmetically acceptable filler, an organic binder and a liquid evaporable carrier in the following amounts by weight to form a slurry:

5	Filler	70%-10%
	Binder	5%-30%
	Carrier	25%-60%
	Coated pigment particles	1%-15%

pouring the slurry into a mold to form a molded product, and evaporating the carrier to reduce the carrier to a residual amount less than 2% by weight of said composition while maintaining said product under atmospheric pressure to form a dried cosmetic powder product.

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